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CONSTRUCTION AND TESTING OF ELECTROCHEMICAL NO_2 PSDs

by

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16. ABSTRACT

The objective of this project was to design, fabricate, test and deliver a prototype portable electrochemical instrument for use as a personal monitor, capable of real-time measurement of low-ppb levels of NO_2. The work was conducted as two distinct tasks that were performed concurrently: (1) improving the currently available NO_2 sensing technology to provide a sensor with sufficiently high signal/noise ratio and stable background signal for continuous low-ppb level measurements, and (2) designing, assembling, testing, and delivering a portable instrument incorporating this sensor technology to provide capability for monitoring personal exposure to ambient NO_2 concentrations.

A very low background, low noise, attitude-insensitive real-time sensor was developed and tested to provide detection of NO_2 at levels as low as 5 ppb. A portable, modular prototype NO_2 monitor was designed and tested. The instrument was interfaced with a commercial data logger to allow collection and storage of real-time concentration data, as well as a continuous display of ambient NO_2 levels. Three of these units were delivered to EPA for evaluation. In addition, preliminary design was completed of a second generation data logger/ controller that can provide optimum ease of use and maximum accuracy.

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliances with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems for air, implementation of agency-wide quality assurance programs for air pollution measurement systems, and supplying technical support to other groups in the Agency, including the Office of Air and Radiation, the Office of Toxic Substances, and the Office of Solid Waste.

This report describes the construction and testing of a personal exposure monitor that uses an electrochemical sensor to provide real time nitrogen dioxide measurements at the parts per billion level.

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ABSTRACT

CONSTRUCTION AND TESTING OF ELECTROCHEMICAL NO_2 PSDs

The objective of this project was to design, fabricate, test and deliver a prototype portable electrochemical instrument capable of real-time measurement of low-ppb levels of NO_2 for use as a personal monitor.

The work was conducted in two distinct tasks that were performed concurrently: (1) improvement of the currently available NO_2 sensing technology to provide a sensor with sufficiently high signal/noise ratio and stable background signal for continuous low-ppb level measurements, and (2) the design, assembly, testing, and delivery of a portable instrument incorporating this sensor technology to provide capability for monitoring personal exposure to ambient NO_2 concentrations.

During this project, the following work was completed:

A very low background, low noise, attitude-insensitive real-time sensor was developed and tested to provide detection of NO_2 at levels as low as 5 ppb. A portable, modular prototype NO_2 monitor was designed, and tested. The instrument was interfaced with a commercial data logger to allow collection and storage of real-time concentration data, as well as a continuous display of ambient NO_2 levels. Three of these units were delivered to PEI (EPA) for evaluation. In addition, preliminary design of a second generation data logger/controller that can provide optimum ease of use and maximum accuracy was completed.

Future work will address further improvement in the NO_2 sensor stability, reduction in NO_2 instrument size, development of the optimum data logger/controller, expansion of the monitor to measure other compounds, and the investigation of multiple-function, multiple-compound, sensor-array based real time monitors.

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SECTION 1

INTRODUCTION

The monitoring of pollutant gases at sub-ppm and low-ppb levels is of primary concern in indoor air and non-industrial locations such as the home. The trend toward more airtight homes, which began during the energy crisis of the early 1970's, has caused concern among health experts about increased levels of indoor pollutants such as the sulfur and nitrogen oxides. It is the objective of this work to develop a personal exposure monitor (PEM) which will allow real-time monitoring of low concentrations of NO_2 in the presence of ambient levels of potential interferents such as NH_3, CO, H_2S, common hydrocarbons, and SO_2.

Several methods are available for the measurement of NO_2 in ambient air. Passive samplers are effective for such measurements and have been in use for several years (1,8). A real-time instrument based upon chemiluminescence reaction with ozone is extremely sensitive (4). However, it is not portable, and interferences make calibration and operation tedious if unambiguous results are desired (3,5). Recent attempts have been made to reduce a chemiluminescence scheme to a portable device (3). Calibration of such systems can also be a challenge and interferences due to other nitrogen compounds occurs (3,4,5).

Amperometric electrochemical sensors provide portable real-time analysis capability and have been used for ppm level measurement of NO_2 (6,7). These sensor systems do not suffer interferences from NO, N_2O, or nitrous acid but often possess too much noise and drift to provide accurate data at ppb levels. Major sources of drift have been tentatively identified as temperature and relative humidity fluxuations (8).

The work discussed in this report has focused upon improvement of the existing electrochemical technique (9,10,11) so that it can be used at ppb levels. This requires gaining an understanding of the reactions of NO_2 in the sensor system. This knowledge is required to design and build an improved real-time portable instrument for the measurement of NO_2 in the field.

The overall objective of this program is to develop a versatile and general approach to the design and construction of real-time personal monitors (PEM) for many airborne pollutants. This specific project is directed to the design, development, and delivery of three personal monitors for the measurement of low levels of NO_2 in ambient air in real time.

In order to accomplish this objective, the work was divided into four specific tasks:

Task 1: Instrument Design

Design and assemble an instrument which includes such features as temperature compensation and software for data acquisition and interpretation.

Task 2: Sensor Optimization

Optimize loading and treatment of sensing electrode and choose electrolyte to provide a maximum signal/noise ratio Fully characterize sensor with respect to artificial response characteristic (sensitivity, linearity, and stability).

Task 3: Construction of Instruments

Engineer and fabricate a portable field unit based upon the results of Tasks 1 and 2.

Task 4: Evaluation of Instrument

Characterize the performance of the instrument against the intended specifications; deliver three units to PEI/EPA for evaluation; and report findings and make recommendations for future work.

Due to the time limitations of the project, TASKS 1 and 2 were performed concurrently using test sensors in the prototype instruments as needed. When instrument design and sensor evaluation tasks were completed, fabrication of the instruments was initiated. The final performance tests of the optimized sensors were conducted in the prototype instruments.

SECTION 2

CONCLUSIONS

Earlier work demonstrated the feasibility of measuring low levels of NO_2 using TRI electrochemical sensor technology (11). The work reported here has implemented the findings and recommendations of the early work and packaged the NO_2 monitoring technology into a modular designed instrument for personal exposure monitoring. Many of the features were successfully implemented such as removal of the mercury battery, a low-noise circuit, and a ten-fold reduction in power consumption. These improvements were accomplished with a simultaneous improvement in the sensing technology such as attitude insensitivity and reduced size.

The work has accomplished interfacing the electrochemical sensor technology with high quality electronics to allow accurate low level measurements and with commercial data logger for unattended exposure monitoring. This PEM system has been characterized and the results are presented in this report.

The three prototype instruments delivered to EPA were subjected to a critical design review at the end of this project and the characteristics and limitations were discussed. The following recommendations came from these discussions.

The sensor performance in this instrument typically provides a signal to noise ratio of greater than 50:1 at 1 ppm, and some sensors possess S/N as high as 200:1. Improvement in several areas of performance are desirable to take full advantage of the sensor's capability. These include reducing the signal drift microphonic signal (spike in signal when sensor it tapped sharply) observed at low concentrations, minimizing the temperature effect upon sensor background and span, and increasing the sensor lifetime.

SECTION 3

RECOMMENDATIONS

At a design review meeting at TRI with EPA officers and potential users, collaborators, and instrument evaluators, TRI presented the results of the project. The discussion led to consideration of many features of the ideal practical personal monitoring instrument. The major directions for the project were defined as a result of this meeting.

Directions and developments to pursue include the following:

1. One module is preferred for field use. Design an instrument package where all three modules are in a single field rugged package.

2. Consider future work in four parts:

   2.a.) improvements to NO_2 hardware and software in collaboration with EPA/RTP such as: evaluations of the technology in a NO_2 chamber to stimulate various field conditions, interface of sensor to EPA diffusion barrier (to possibly eliminate the pump and reduce instrument size and weight), investigate options for a rapid temperature sensor and small RH sensor that will accurately compensate the NO_2 sensor; and survey ultra-low-power op-amps to further reduce weight of the power pack.

   2.b.) design and incorporate a true data logger and instrument controller into the instrument (hardware & software). This will allow the attainment of maximum sensitivity and accuracy for the instrument in field situations and maximum integrity of the scientific data to be collected.

   2.c.) consider expansion of the real-time PEM approach to other gases such as CO, hydrocarbons, and other toxic vapors.

   2.d.) investigate designs for a multi-function multi-compound sensor array type instrument for field use that will increase the efficiency, accuracy, and reliability of field measurements.

3. Perform complete laboratory and field evaluation of the existing technology.

4. Redesign pump circuit for control by μ-processor and minimize pump power consumption to allow automatic zero adjust and elimination of a major source of error in the field (zero drift).

5. Place temperature sensor within NO_2 sensor housing for more accurate compensation and improved accuracy in the data. Also, consider sensor designs that are independent of temperature.

6. Write custom software for μ-processor controller/logger to include features important in field exposure monitoring such as real-time display, event marker, and simple data retrieval.

7. Fabricate smaller more rugged (molded) sensor to allow smaller instrument design and extended lifetime sensor.

8. Design a CO sensor to expand instrument application.

9. Develop a sensor array to expand the number of gases that can be monitored and the accuracy and reliability of the personal monitoring instrumentation.

SECTION 4

EXPERIMENTAL

All gases and gas mixtures were supplied by Scott Specialty gases in pressurized cylinders at a concentration of 49-400 ppm NO_2 in air. Working standard mixtures of NO_2/air were prepared fresh several times daily by dilution of the stock gas mixture. Low levels of NO_2 in air were prepared using a calibrated permeation device (KinTek Laboratories, Houston, TX). All mixtures were NO_2 in laboratory air unless otherwise defined.

Deionized H_2O and reagent grade chemicals were used throughout the project. Noble metals for electrodes were obtained as 99.999% pure from Englehard Minerals and Chemicals Company. All sensor and pneumatic parts (fittings and tubing) that contacted the sample were made of inert materials (either polypropylene, Tedlar, polyethylene or Teflon).

Gas flow through the sensor was controlled using Spectrex AS-400 pumps and Matheson Model 602 (0-1L) and 603 (0-5L) flow meters fitted with clippard needle valves. Elevated temperature experiments were conducted in a GCA/Precision Scientific Model 18 oven. Low temperature experiments were performed in a modified GE TA242TH refrigerator. Temperature was monitored with a 0-110^{o}C mercury thermometer to the nearest degree Celsius.

Circuit board production and assembly was performed by Trescomp, Inc., a local (small minority-owned) electronic design and assembly firm in the suburban Chicago area. Engineering design changes were recommended by Trescomp and implemented as appropriate.

Commercial sensors were obtained from the Energetics Sciences Division of National Drager (ND or ESI sensors). Solid electrolyte sensors using Nafion (EI Du Pont trademark) cation exchange material and aqueous electrolyte sensors with low surface area (LSA) and high surface area (HSA) catalysts on porous membranes were designed and built by TRI under carefully controlled conditions.

Sensors were tested in the "pump-after-sensor" gas flow configuration recommended in earlier work (11). A low volume exposure chamber was used to test the ND sensors. The volume of the chamber used with the TRI sensors was decreased by 50% from prior work (11) in order to increase the linear flow rate of analyte past the working electrode. This design change should improve response time and signal magnitude.

All of the bench-top experiments were performed at room temperature (approximately 22 ^{o}C) and the potential of the NO_2 gold sensing electrode was maintained constant at + 800 mV vs. SHE (-200 mV VS. Pt/air reference electrode) throughout the tests. The sample (analyte) flow was 100 cc/min through the sensor and, since the gas mixtures were prepared from laboratory air, most tests were performed at 30-60% RH. Only tests of the 49 ppm NO_2/air commercial mixture were dry ("approximately" 0% RH).

SECTION 5

RESULTS AND DISCUSSION

The results for each of the tasks described in Section 1.0 are presented and discussed in this section.

PROTOTYPE INSTRUMENT DESIGN

The Ideal Instrument

The first step in designing the NO_2 instrument was to list all the capabilities which would be desired in an "ideal" personal monitor for NO_2. These specifications are listed in Table 1 and form a specific focus for the remainder of the effort. Using an optimum electrochemical sensor technology will allow some but perhaps not all of these objectives to be reached within the scope of this project. Certain capabilities, such as auto-zero adjust, required that a custom integrated data logger and instrument controller be designed in the unit. The data logger task will not be addressed until Phase II of the project and, therefore, provision for this capability is made but cannot be implemented until the next project Phase (FY88).

The "ideal" instrument (proposed after discussion with project personnel at the start of the project) possessed a modular design. It consisted of three parts:

(1) sensor or NO2 instrument module for measurement of real-time concentrations,

(2) data logger and μ-P (microprocessor) control module, and

(3) power pack.

The list of features given in Table 1 was used as the starting point for designing an instrument which would be modular in design. The data logger unit was postponed to FY88 but provision for its inclusion into the prototype PEM has been made.

The major challenges in the work included:

1) discover a microprocessor-based data-logger which possessed the required desired characteristics so that the unit could be used and tested after Phase I (before completion of the custom data logger unit in FY88),

TABLE 1: IDEAL NO_2 INSTRUMENT DESIGN GOALS

MODULAR CONCEPT - THREE MODULES

MODULE 1 - REAL-TIME NO_2 MONITOR

Type: Real-time, continuous NO_2 monitor.

Operating Time (fully charged Ni-Cds):
Standby ≥ 24 hrs
Run ≥ 24 hrs electronics and 24 hrs pump
Run continuous using AC adapter

Range: 0-1 to 0-50 ppm

Sensitivity: lower detection limit ≤ 6 ppbv NO_2 in air.

Zero-measurement: performed automatically under micro-processor control, at specified intervals.

Response Time(0-90%): <60 sec

Recovery Time (100-10%): <60 sec

Reproducibility: better than ± 5% over 8 hrs.

Sensor background noise: <5 ppbv

Background: < 0.1 - 0.25 ppmv

Stability: Zero Drift - ≤ 20 ppb/8 hrs
Span Drift - ≤ ± 5% F.S./8 hrs.
Temperature Drift - temperature compensated.

Humidity Range: 5-95 %

Sensor Lifetime: 1 year (> 6 months continuous use).

Interferences: ≤ 15 ppb for all common vapors.

Versatile: easily adapted to additional compounds and situations.

TABLE 1 - CONTINUED

MODULE 2 - Data Logger/CONTROLLER

I/O Configuration:

1) 8 Digital I/O channels.
2) 8 analog input channels, including:
   i) (one) Temperature measurement
   ii) (seven) ±2.5 V data channels
3) Input voltage from any probe with impedance >10kΩ

Microprocessor:

4) 12-bit resolution (resolve 0.1% of readout)
5) 32-128 Kbyte RAM (enough for 60,000 data points)
6) Programmable in high level language (C or Basic); floating point precision;
7) >16K non-volatile RAM; protects data when battery fails
8) Storage: 1pt/sec = 86,400pts/day, one channel
   21,600pts/day, four channel
   (With compression, unlimited storage)
9) RS232 port (interface with IBM-type PC; 1200 baud min.
10) Event marker, automatic or manual.
11) Real time clock

Physical parameters:

12) Battery operation; 6 mo., 9V (30 days, rechargeable)
13) Room for system monitor/malfunction LED's.
14) Size: small (<16 oz., approx. 2"x4"x6")
15) Temperature range of -10°C to +60°C.

MODULE 3 - POWER PACK

Sufficient to meet the operating requirements of module 1 and module 2. In addition, the power pack should be small, use rechargeable and/or common alkaline batteries, have a single plug type connector, and be interchangeable with an AC adapter so that portable or fixed-site continuous operation is possible.

==========

==== NOTE ==== AN ALTERNATIVE OPTION FOR INSTRUMENT DESIGN WAS CONSIDERED AFTER THE PROJECT REVIEW ON 12/3/87. AT THIS TIME, SINCE ALL THREE MODULES TURNED OUT TO BE RELATIVELY SMALL, A VIABLE OPTION BECOMES THE DESIGN OF ALL THREE MODULES INTO A SINGLE UNIT. THIS WORK WILL BE ADDRESSED IN FY 88 TASKS.

2) package all the electronics and hardware into minimum volume and maintain the desired functions for true personal exposure monitor, and

3) attain signal/noise and signal/background performance capability of the NO_2 sensor and instrument at low ppb levels in the portable instrument system while operating on a battery.

The advantages of the proposed modular design include greater flexibility (e.g., easy modification of the NO_2 monitor portion for other gases), smaller size for each module, and more functions per module (e.g., module can be used with other data logger systems). Disadvantages of modular construction include: larger overall size, interconnections, and tendency only to lose or misplace separate components. For this initial FY87 work, the advantages of the modular design appeared more important than therefore, included the initial evaluation of the instrument capabilities in a modular design. In this way, as the research progresses, changes and revisions can be made easily to each circuit as required. In addition, modular may be made to interface with existing commercial equipment. Thus, field testing and lab evaluation of the NO_2 sensor can begin much earlier in the project.

The Proposed Instrument

After discussion of the specifications of ideal instrument, the hardware designs for the NO_2 instrument were prepared. A block diagram of the NO_2 unit is shown in Figure 1. The components of the instrument were identified as:

1. Pump/sensor - module 1: This component would be the center of the unit. It would contain the sensor, pump, potentiostat circuit, pump motor control circuit, circuit to provide a stable power supply, temperature circuit, and all signal measurement circuits. There would also be provision for an alarm circuit and LED display for continuous readout but this would not be included in the prototype instruments.

2. Data logger/controller - module 2: This component of the unit would consist of the A/D channels for signal input and D/A output channels for instrument control. The input channels would monitor the sensor output, temperature, battery voltages, sensor bias, and other pertinent parameters. The output channels would allow control of the pump motor circuit and analog switch for auto-gain set and auto-zero measurements. An evaluation of existing and possible data loggers relative to these specifications was completed as a part of this work.

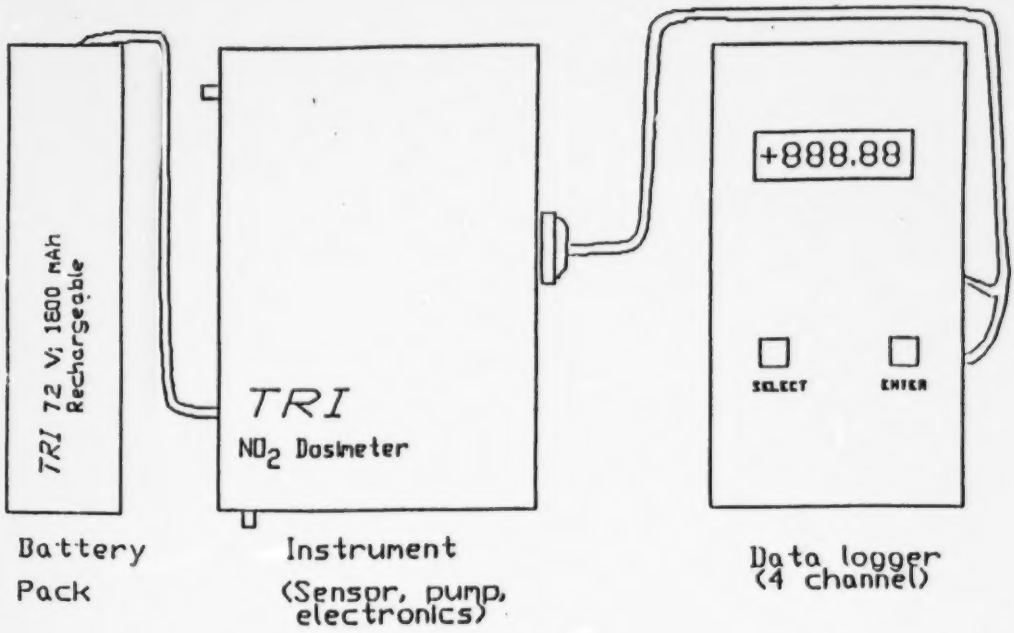


Figure 1: Conceptual layout of NO_2 Real-Time Instrument. Data logger allows real-time display of NO_2 levels, as well as logging of data for later transfer to personal computer for analysis.

3. Battery pack - module 3: This module would contain the rechargeable Ni-Cad batteries used for pump power. To provide the voltage to operate the pump motor circuit as well as power the pump, a 7.2 V pack would be needed. A 9 V battery would be included in module 1 to keep the sensor on standby and ready for use even when the instrument was not deployed.

The result of this design task included a work schedule to:

1) Design and deliver three working modular NO_2 units, and

2) Design a microprocessor controlled datalogger/controller which will be fabricated in a future task (FY88).

ELECTROCHEMICAL (AMPEROMETRIC) SENSOR DEVELOPMENT

Results of earlier work (11) indicated that the best sensor response at sub-ppm levels would be obtained from a three electrode sensor using a low surface area (LSA) sensing electrode. The design of this type of sensor is illustrated in Figure 2. The two types of low surface area sensing electrodes considered by TRI consist of a powder pressed onto a Nafion cation exchange membrane and metal vapor deposited onto a porous membrane. The Nafion sensor was evaluated in earlier work (11).

TRI has obtained excellent response from catalyst films vapor deposited onto porous membranes. By controlling the nature of this film, the signal can be optimized. Commercially available high surface area (HSA) sensors and the TRI Nafion sensor were used as "performance standards" for evaluation of the "improved" responses from the TRI LSA sensors tested in this work.

Due to the improvements in electronics and sensors (11) the TRI sensor has a very high signal to noise ratio. The response, therefore, is not limited by sensor noise or circuit noise. It was anticipated that the major limitation on lower detection limits would be due to baseline (or zero) drift of the sensor. This drift occurs primarily due to environmental fluctuations (T, P, RH) and the presence of interferences. Therefore, a major requirement for the instrument is the ability to periodically re-zero, or at least perform a measurement of the background signal. It is also highly desirable to monitor temperature, since temperature variations can cause drift. Measurement of the temperature will allow precise compensation of both zero and span for any calibrated electrochemical sensor used with the unit. This is accurate calibration since the user does not "assume' a temperature coefficient for a sensor but us able to measure it.

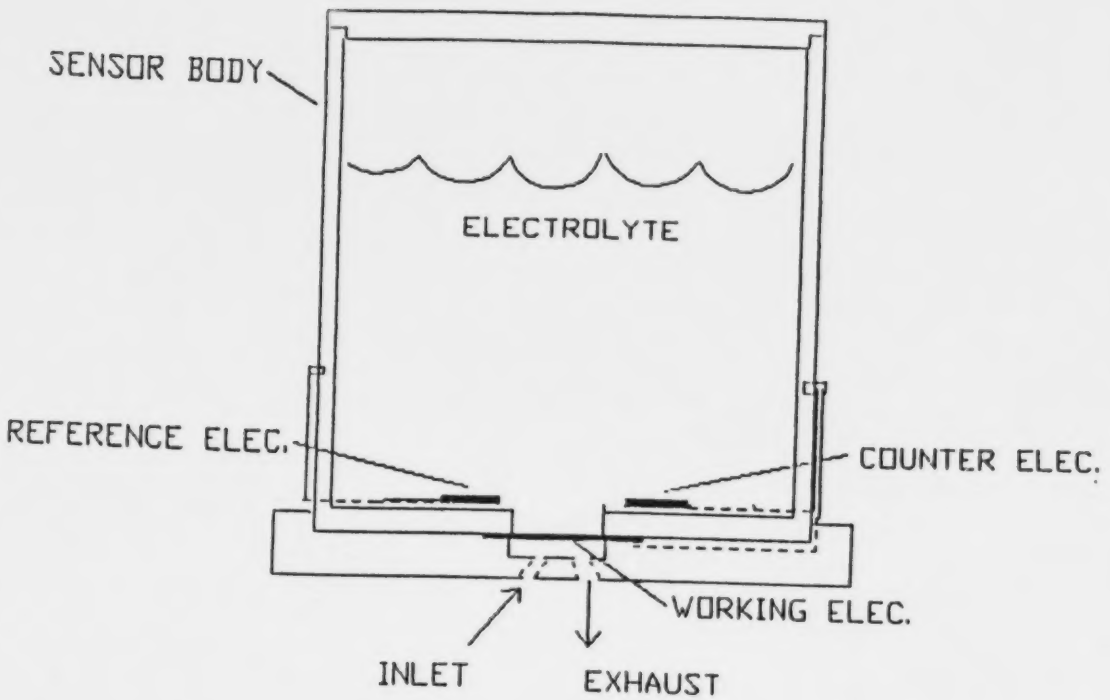


Figure 2: Diagram of standard TRI electrochemical sensor.

Membrane Selection:

Choice of a membrane for the sensing electrode is critical and the membrane can have a profound effect upon analytical performance. For use in a personal monitor, it is necessary that the membrane be rugged and possess a very high resistance to water flow through the pores. A series of tests were performed to compare the properties of several porous membranes to determine the one most suited for the NO_2 monitor. The membranes tested included porous polypropylene (CG 4400 and CG 4500), porous Teflon films on polypropylene backings (Gortex, G-1 μm and G-0.45 μm), and the woven porous Teflon sheet (Z-606-223, Z-606-122, Z-662-123, G-104, and G-110).

The membrane properties evaluated included tensile, or tare, strength, porosity, weeping pressure (the pressure required to force electrolyte through the membrane), and response characteristics. Table 2 summarizes the technical data and test results for these materials. Several of the membranes tested provide suitable substrates. The Gortex (0.45 μm and 1.0 μm pore size), Celgard (0.02 and 0.04 μm) as well as the Zitex material (E606-122 and E606-223) were tested in TRI sensor designs.

Catalyst loading:

The magnitude of the signal from a given concentration of analyte gas is proportional to the catalyst loading on the membrane until the reaction rate is no longer catalyst limited. The optimum loading for a sensor is the one that produces constant response and slight variations in catalyst activity (due to small changes in temperature or specific surface area) do not substantially affect the sensor signal.

A series of tests were performed to establish the relationship between catalyst loading and sensor response to NO_2 for each of the potential membrane materials. All catalyst films were placed upon the membranes using ultra high purity metal catalyst and vacuum vapor-deposition techniques. The first experiment evaluated different candidate low surface area (LSA) sensing electrodes. These included the three porous membrane materials above and several catalyst loadings for each membrane: 600, 900, 1200, 2100, and 3000 Angstroms. The array of sensors constructed from the different electrode and membranes were evaluated for signal magnitude (μA/ppm), background current (ppm), noise level (ppb), and response time.

The results of the initial sensor performance tests are shown in Table 3 and Figures 3-5. The sensor background and response is plotted as a function of catalyst loading on the various membrane as shown in Figure 3. All of the materials except the G-1.0 yield a maximum signal at 2100 Angstroms. It is not clear why the signal becomes smaller at higher loadings,

TABLE 2: Physical Properties of Porous Membrane Materials

MATERIAL	COMPOSITION	TENSILE STRENGTH (lb/in)	WEEPING PRESSURE (mm Hg)	THICKNESS (mm)	PORE SIZE (μm)	POROSITY (%)
Gortex	TFE Teflon	--	>525	.1016	0.45	84%
(G-1.0)		--	525	.0508	1.00	91%
Celguard						
CG4400	Poly-	1.0 lb	>550	.025	0.02	38
CG4500	propylene	1.0 lb	>550	.025	0.04	45%
E606-122	TFE Teflon	0.5-1.2	---	.14	5-10	---
E606-223		1.4-2.8	---	.18	2-5	---
H662-123		0.9-1.8	---	.20	10-20	---
G104		4.8	---	.1016	5-6	---
G110		12.0	300	.254	1-2	---

TABLE 3: Results of catalyst loading and membrane material evaluation studies.

Gortex						
2ppm NO2	LOADING	S(uA/ppm)	B.G.(uA)	S.R.(sec)	S.D.(sec)	
	600	0.10	0.10	50	15	
	900	0.145	0.06	15	15	S. decay
	1200	0.10	0.03	15	60	Noise
	2100	0.22	0.04	15	15	S. decay
	3000	0.29	0.04	15	15	S. decay
5ppm NO2	600	0.092	0.04	60	15	
	900	0.16	0.10	15	15	S. decay
	1200	0.118	0.10	15	15	
	2100	0.22	0.075	15	15	
	3000	0.29	0.025	15	15	

Zitex 223						
2ppm NO2	LOADING	S(uA/ppm)	B.G.(uA)	S.R.(sec)	S.D.(sec)	
	600	0.021	0.17	15	30	Noise 1 nA
	900	0.045	3.70	15	15	B.G. drift
	1200	0.037	0.05	15	15	
	2100	0.055	0.55	15	15	S. decay
	3000	0.017	0.075	15	30	Noise 1nA
7.3ppm NO2	LOADING	S(uA/ppm)	B.G.(uA)	S.R.(sec)	S.D.(sec)	
	600	0.016	0.120	30	30	Noise 1 nA
	900	0.038	3.70	20	60	B.G. drift
	1200	0.036	0.04	20	20	
	2100	0.040	0.70	20	20	S. decay
	3000	0.018	0.060	30	30	Noise 1nA

(4400) Celgard +122						
2ppm NO2	LOADING	S(uA/ppm)	B.G.(uA)	S.R.(sec)	S.D.(sec)	
	600	0.083	0.005	180	15	
	900	0.078	0.290	15	15	BG drift .05mV/min
	1200	0.108	0.40	15	15	BG drift .086mV/min
	2100	0.142	0.095	20	15	
	3000	0.075	0.08	15	15	
7.3ppm NO2	LOADING	S(uA/ppm)	B.G.(uA)	S.R.(sec)	S.D.(sec)	
	600	0.074	0.01	15	15	
	900	0.082	0.260	15	15	
	1200	0.11	0.37	30	30	
	2100	0.135	0.10	20	20	
	3000	0.075	0.08	15	15	

TABLE 3 (continued)

(4500) Celgard +122

2ppm NO2	LOADING	S(uA/ppm)	B.G.(uA)	S.R.(sec)	S.D.(sec)	
	600	0.032	0.005	40	40	
	900	0.045	0.025	15	25	Noise 0.5 nA
	1200	0.172	0.14	25	20	
	2100	0.232	0.006	15	15	S. drift
	3000	0.042	0.028	30	30	

7.3ppm NO2	LOADING	S(uA/ppm)	B.G.(uA)	S.R.(sec)	S.D.(sec)	
	600	0.023	0.032	40	30	
	900	0.036	0.012	70	240	
	1200	0.103	0.03	15	20	S. very nice
	2100	0.129	0.005	15	15	S. very nice
	3000	0.028	0.040	60	70	

Gortex 0.45: Gortex porous Teflon, with 0.45u pores.
Zitex 223: Zitex E606-223 Porous Teflon, 2-5u Pores.
Celgard 4400: Celgard Polypropylene Membrane, 0.02u Pores
Celgard 4500: Celgard Porous Polypropylene, 0.04 u Pores

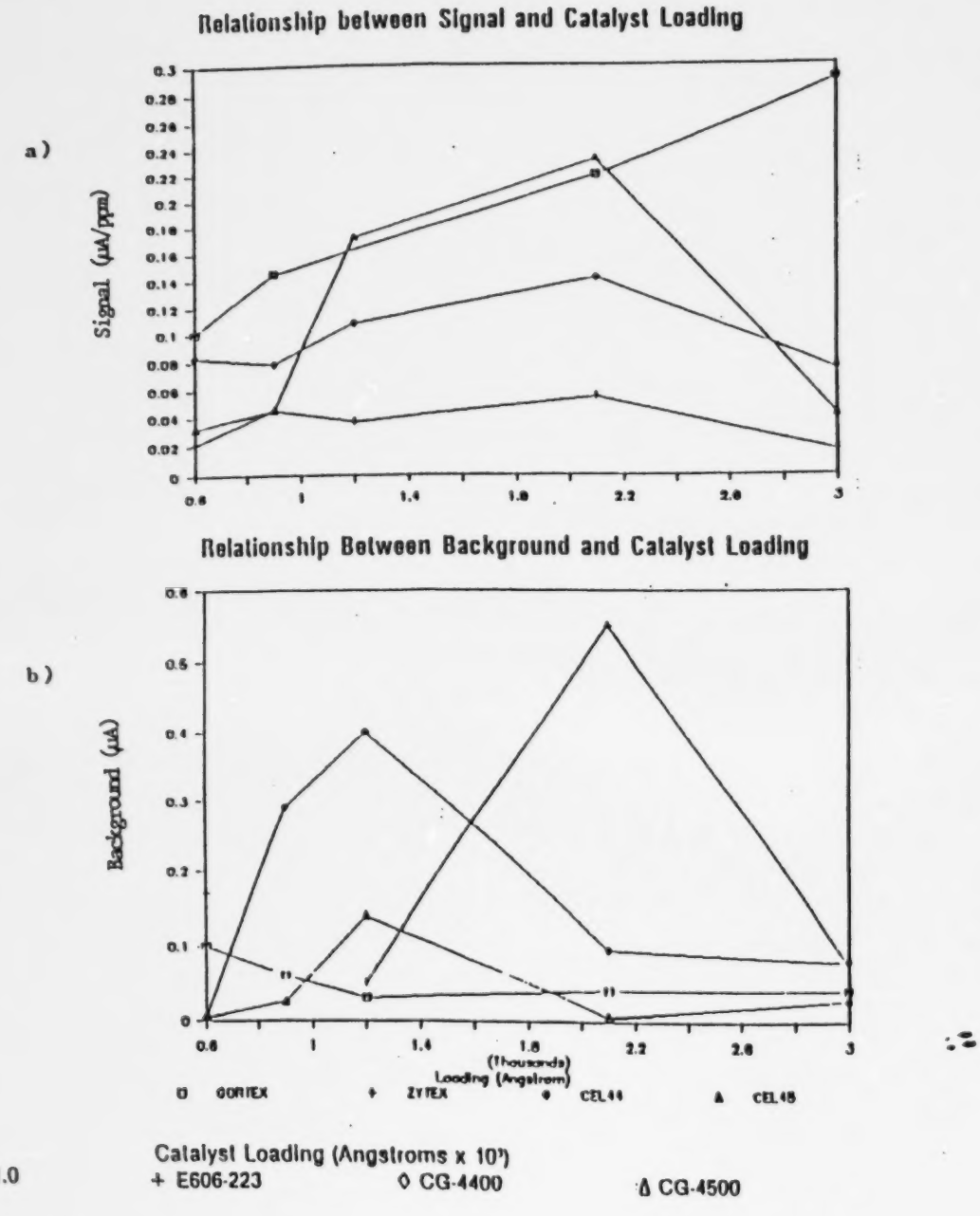


Figure 3: Response characteristics of sensors using different membrane materials and catalyst loadings.
a) Sensitivity to NO_2 at 2 ppm.
b) Sensor background current.

although it is possible that, for the CG-4500 material (0.04μm pore size), the gold thickness has become sufficient to partially fill the pores. The G-1.0 membrane signals, however, are still increasing with loading at 3000 A. In Figure 4, representative NO_2 responses are illustrated for three different membranes. Catalyst loadings are 2100 Angstroms for Figures 4a and 4b and 7.3 mg/cm_2 in 4c.

The G-1.0, G-0.45, GC-4400, and CG-4500 membrane sensors have the fastest response and largest signal, with 1200-2100 Angstrom loadings providing the optimum results. All of the TRI sensors yield an extremely low background current and noise level when compared to commercial (HSA) sensors (see Figure 5).

The G-1.0 LSA sensor yields a signal of approximately 0.1-0.3 μA/ppm, with typical background currents of 0.05-0.5 ppm. The noise levels of >5 μA corresponds to approximately 5 ppb NO_2.

The G-1.0/2100, CG-4500/1200 and CG-4500/2100 sensors were selected for further evaluation. Also chosen for these tests was a TRI sensor having a HSA powder catalyst loading of 7.5 mg/cm^2 on E606-223 membrane. This HSA sensor was selected as a reference, with performance expected to be similar to commercial high surface area electrode sensors. This set of tests include an evaluation of the signal size with concentration, temporal stability, repeatability or precision, temperature effects on zero and span, and flow rate effects on sensor sensitivity. All three LSA sensors, as well as the HSA sensor, exhibited a response magnitude that is linear with concentration to at least 50 ppm NO_2/air (Figure 6). Although the CG membrane exhibited a slightly faster response time, the G-1.0 membrane produced a substantially higher signal.

Based upon the signal size and physical properties of the G-1.0 membrane, it was chosen as the most suitable membrane for the sensor. Initial tests of the reproducibility and stability of sensors using this material were encouraging. Precision of the sensor response was typically within ± 5%, and baseline drift less than 20 μA,(> 100 ppb) over 4 hrs of testing at 1-5 ppm NO_2 levels. The data indicate that the performance of the sensor could be improved even further with a higher loading of electrocatalyst.

Bias vs. Signal:

The potential of the sensing, or working, electrode (called the sensor bias voltage or simply bias) will affect both the sensitivity and the selectivity of the sensor. It is therefore possible to adjust the bias so that interferences are minimized and response is maximized. Several sensor bias voltages were tested to determine the most useful bias for the intended application. This work confirmed earlier studies (11) and the

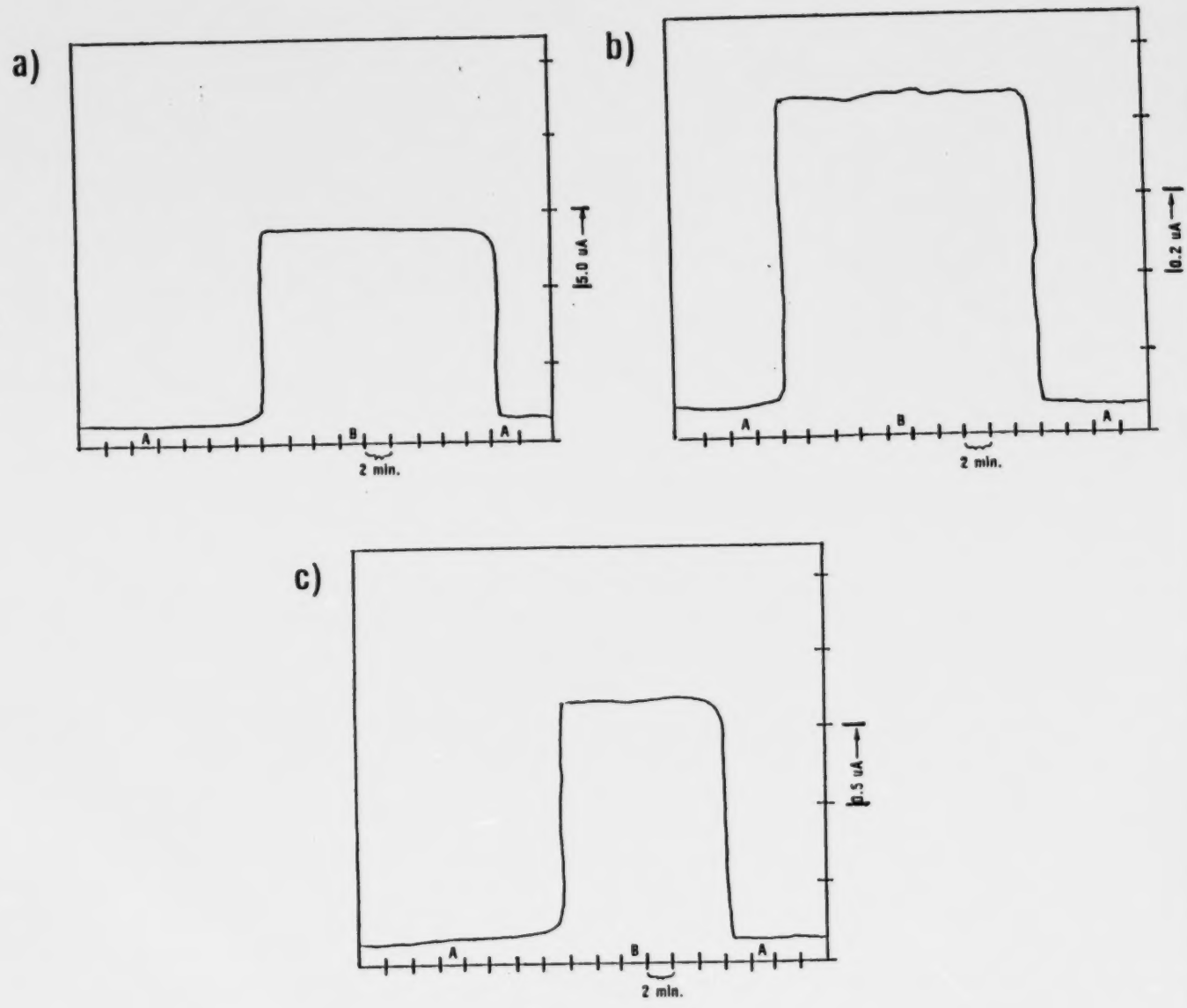


Figure 4: Typical responses of TRI sensors using the three types of membrane materials. (A = Background, B = signal).
a) G-0.45; 49.2 ppm NO_2 b) CG-4400; 7.3 pp.m. NO_2 c) E606-223; 11.5 ppm NO_2

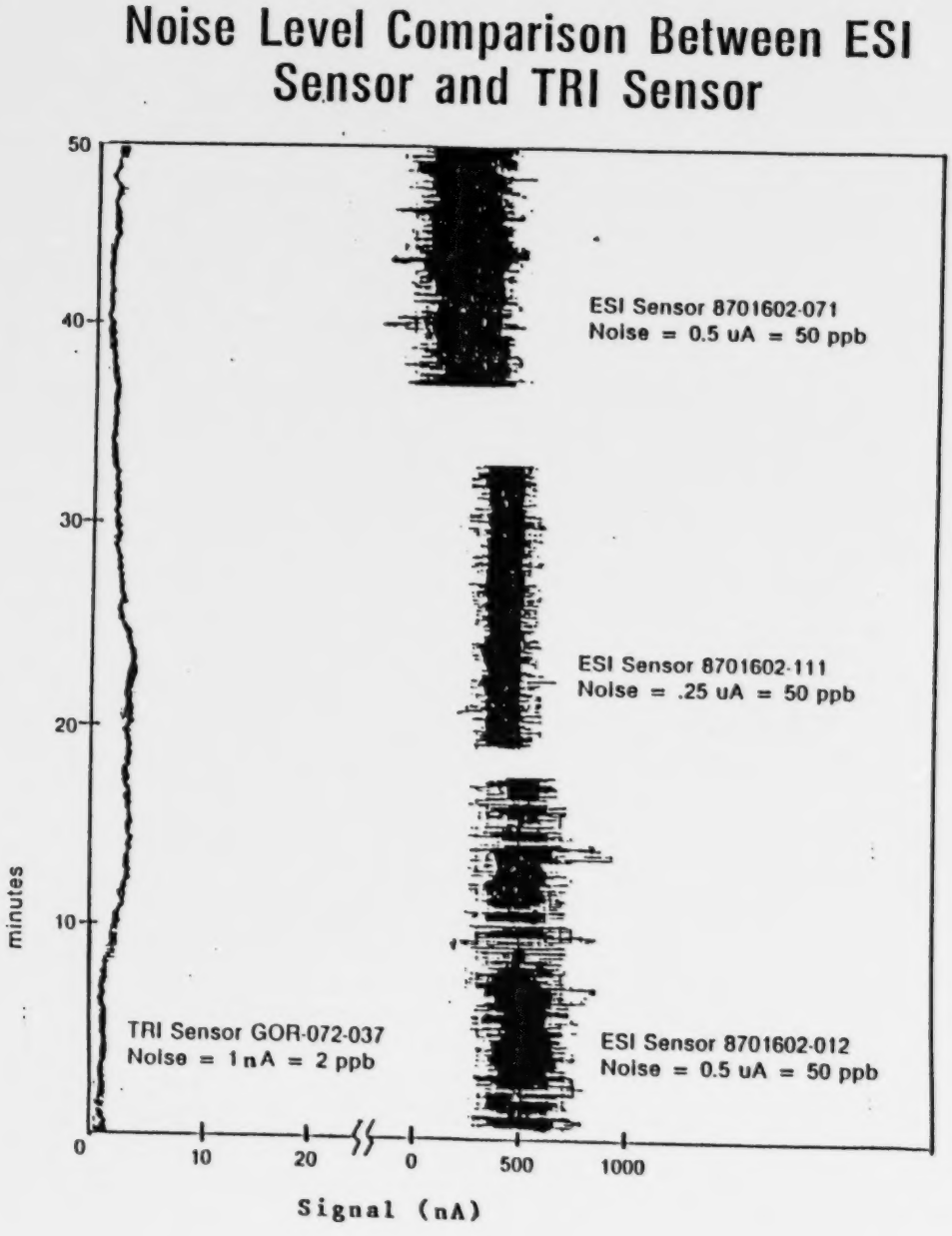


Figure 5: Relative background and noise for commercial HSA sensor and TRI LSA sensor.

EPA NO_2 Sensor Linearity Test

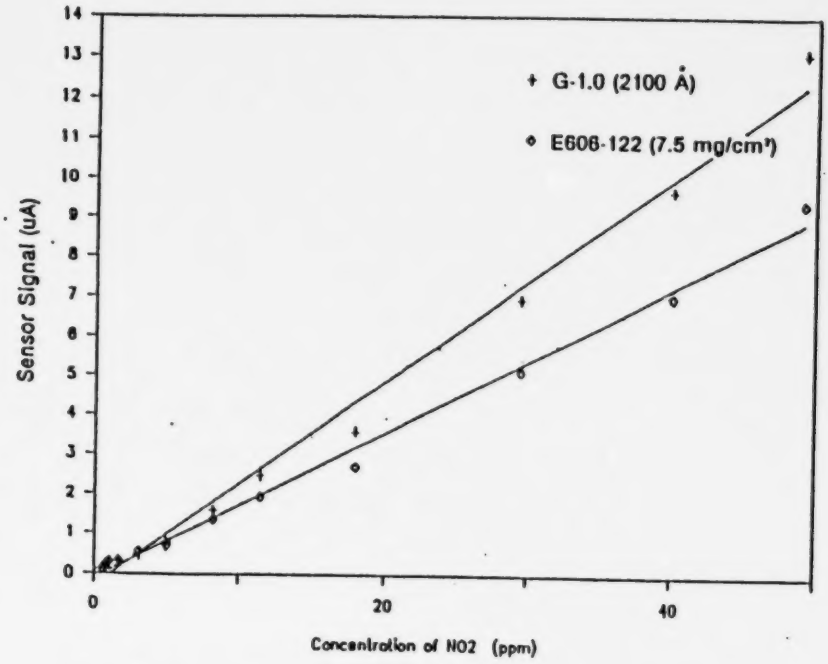


Figure 6: Response for 0-50 ppm NO_2 on Porous Teflon

optimum bias for this system is between -100 and -200 mV versus the Pt air reference electrode for NO_2 sensing. For the aqueous electrolyte sensor, the signal/BG ratio is also a maximum at about -200 mV bias for this particular sensor system.

In order to use the sensor for a portable monitor, it is necessary to make it position and attitude insensitive. An hydrophilic polypropylene wicking material was packed behind the sensing electrode membrane so that it extended down into the electrolyte. This wick insures continuous contact between the sensing electrode and the electrolyte; even if the sensor were turned upside down. The final configuration used in the sensors fabricated for use in the instruments is shown in Figure 7 and the presence of the wicking material provides adequate contact between the electrodes and electrolyte.

Based upon the data from the optimization study described above, several optimized sensors were constructed for testing in the personal monitors.

CHARACTERIZATION OF TRI NO_2 SENSOR

A series of tests were performed to characterize the response of the new TRI sensor in the configuration (membrane plus catalyst loading) described above. These tests included evaluation of the following characteristics:

Signal Magnitude and signal/noise at ppb levels
Effect of flow rate
Effect of temperature
Reproducibility or precision of response
Long term stability (sensor lifetime)
Selectivity (CO, H_2S, and other common interferences)
Attitude-sensitivity of signals

Signal Magnitude:

The signals for the TRI LSA sensor were compared to those of a TRI Nafion electrolyte sensor and a commercially available HSA sensor (the ND sensor) and the comparison is illustrated in Figure 8. The improvements realized in the signal/background with the LSA sensor should allow the optimum monitoring for NO_2 at the lowest levels. However, the versatility of the monitor will allow use of all these sensors in the unit. The HSA sensors may provide a better response at extremely high levels of pollutant while the LSA sensors are optimized for performance at low concentrations.

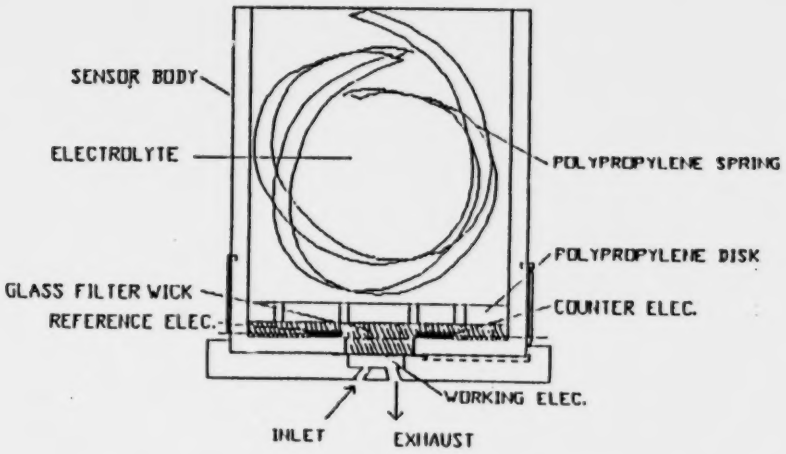


Figure 7: Design of TRI attitude insensitive sensor, noting placement of wick and spring to hold wick in place.

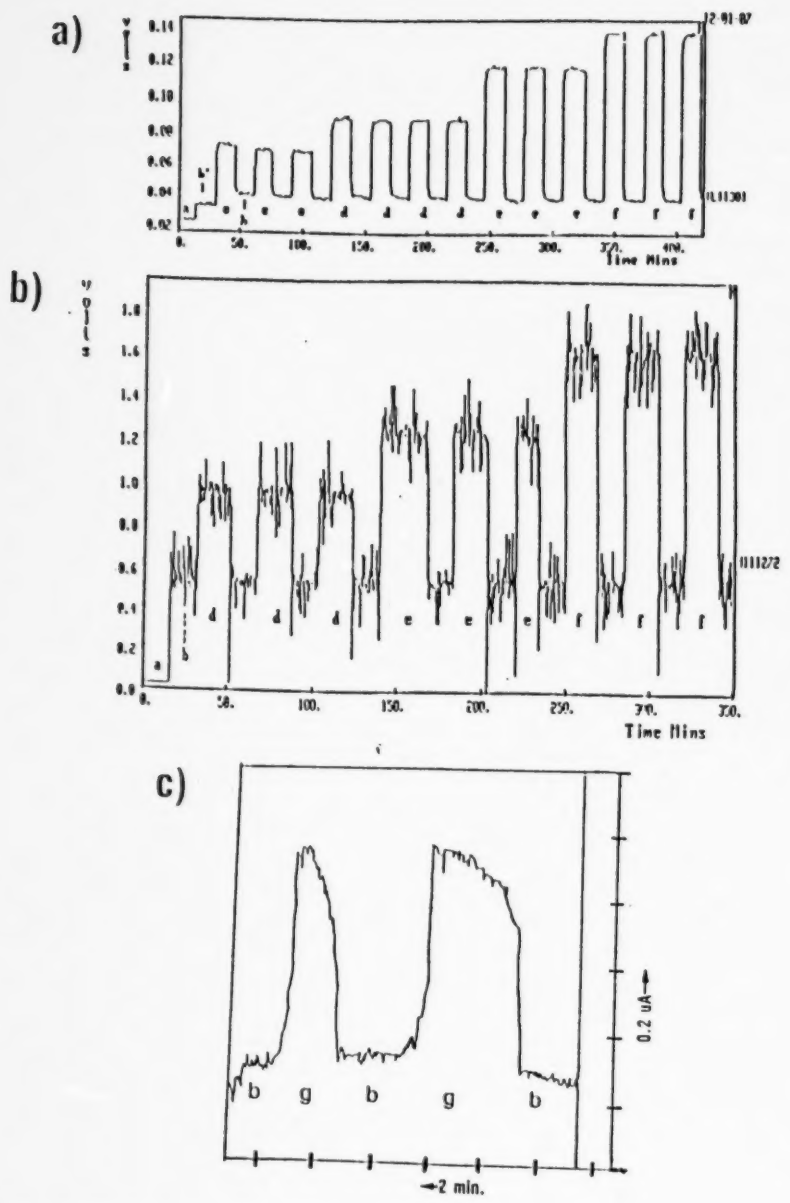


Figure 8: Response of a) TRI LSA sensor, b) commercial HSA sensor, and c) TRI Nafion sensor to ppb levels of NO_2. In 8a and 8b, b = Background, c = 117 ppb, d = 234 ppb, e = 351 ppb, f = 515 ppb. In 8c, g = 100 ppb.

Effect of Flow Rate:

For a sensor operated in a flowing air stream, it is necessary to determine the effect of the rate of air flow upon the response of the sensor. Ideally a sensor would be independent of air flow, at least in the range likely to be encountered during operation of the instrument. The HSA and LSA sensors were tested over a range of flow rates, with the results shown in Figure 9. The commercial sensor (actually designed to be operated in the diffusion mode and at higher concentrations) is independent of flow rate over a wider range than is the LSA sensor. However, the LSA sensor is independent of flow rate in the range 45-300 cc/min. Since the air flow will be set at 100 cc/min, any fluctuations in pump speed will not affect the response of the sensor (for either sensor).

Effect of Temperature:

The greatest source of error in the measurement of NO_2/air concentrations with the sensor result because of drift of the sensor background (zero) and sensitivity (span). The effect of temperature on the sensor performance was studied and Figure 10 illustrates the data for background current vs. temperature for two LSA sensors. The background signal varies as a function of the square the temperature measured in degrees Centigrade. For the sensors studied, the background increased from 0.1 μA at 4^{o}C to 0.4 μA at 45^{o}C. This background drift due to temperature changes is approximately 10 ppb/^{o}C.

If the rate of reaction of the analyte gas is limited by the active working electrode surface area, then the temperature will have an effect upon the sensitivity of the sensor (or span in the instrument. It was expected that the LSA sensor, would be exhibit substantial temperature sensitivity and this is confirmed by the data collected for several LSA sensors at several temperatures. As illustrated in Figure 11, the sensitivity, expressed in μA/ppm NO_2, increases with temperature from 3^{o}C to 47^{o}C. A slope of 0.01 and 0.004μA/ppm was observed for sensors TRI#140 and TRI#120, respectively. This corresponds to about 10 and 20 ppb/^{o}C, respectively. The NO_2 designed to collect temperature data as well as sensor signal to provide accurate compensation of data.

There are at least two methods of correcting sensor response for temperature effects. The most common method is to install electronic compensation by including in the potentiostat gain circuit a component whose temperature coefficient is the inverse of sensor being used. The two responses should then cancel to electronically correct the signal and minimize the temperature effect. To utilize this method the sensor must remain stable over its lifetime and new sensors must be identical to old sensors.

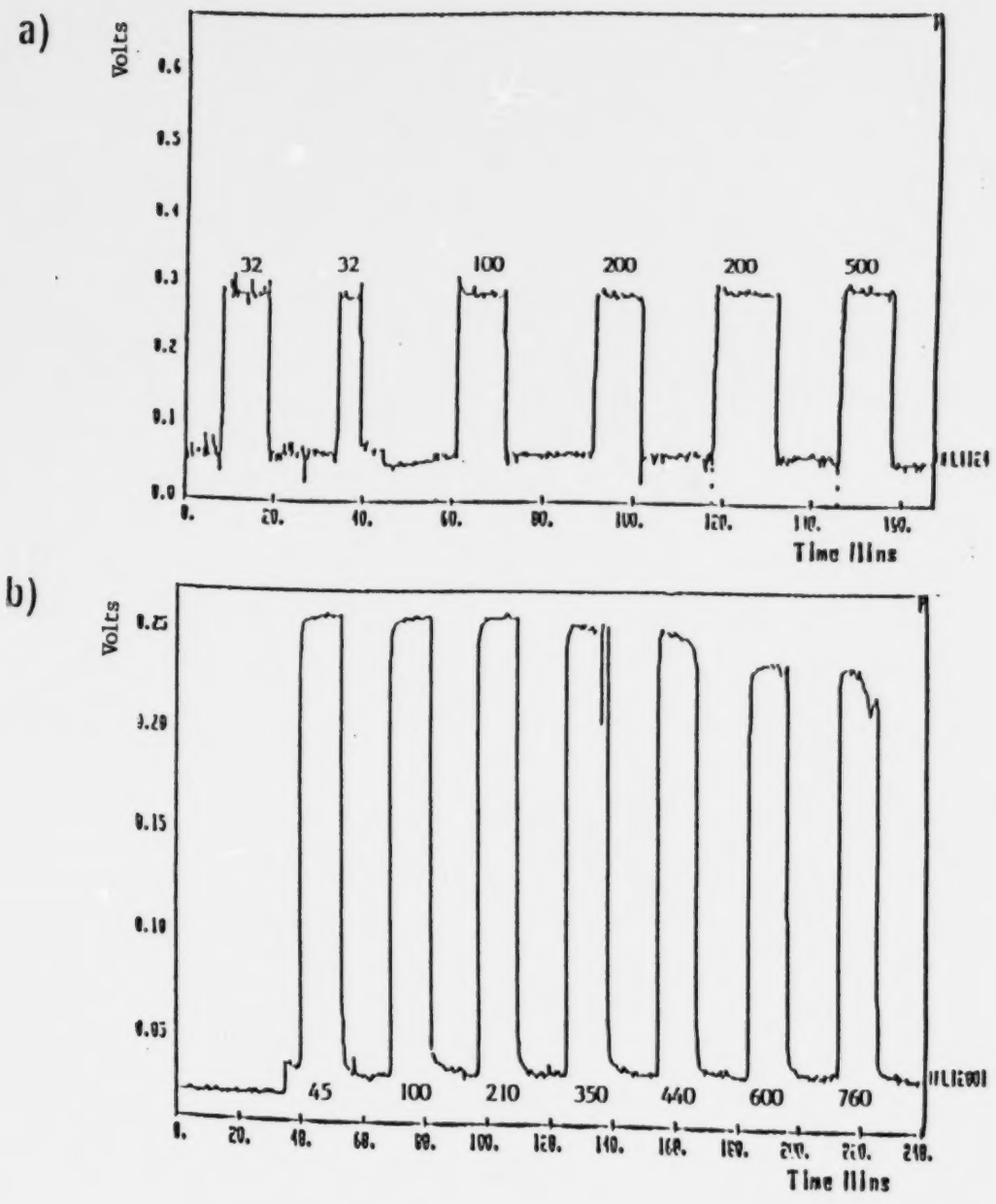


Figure 9: Response versus flow rate
a) Commercial sensor; 1 ppm NO_2; 32-500 cc/min.
b) TRI sensor; 1 ppm NO_2; 45-750 cc/min.

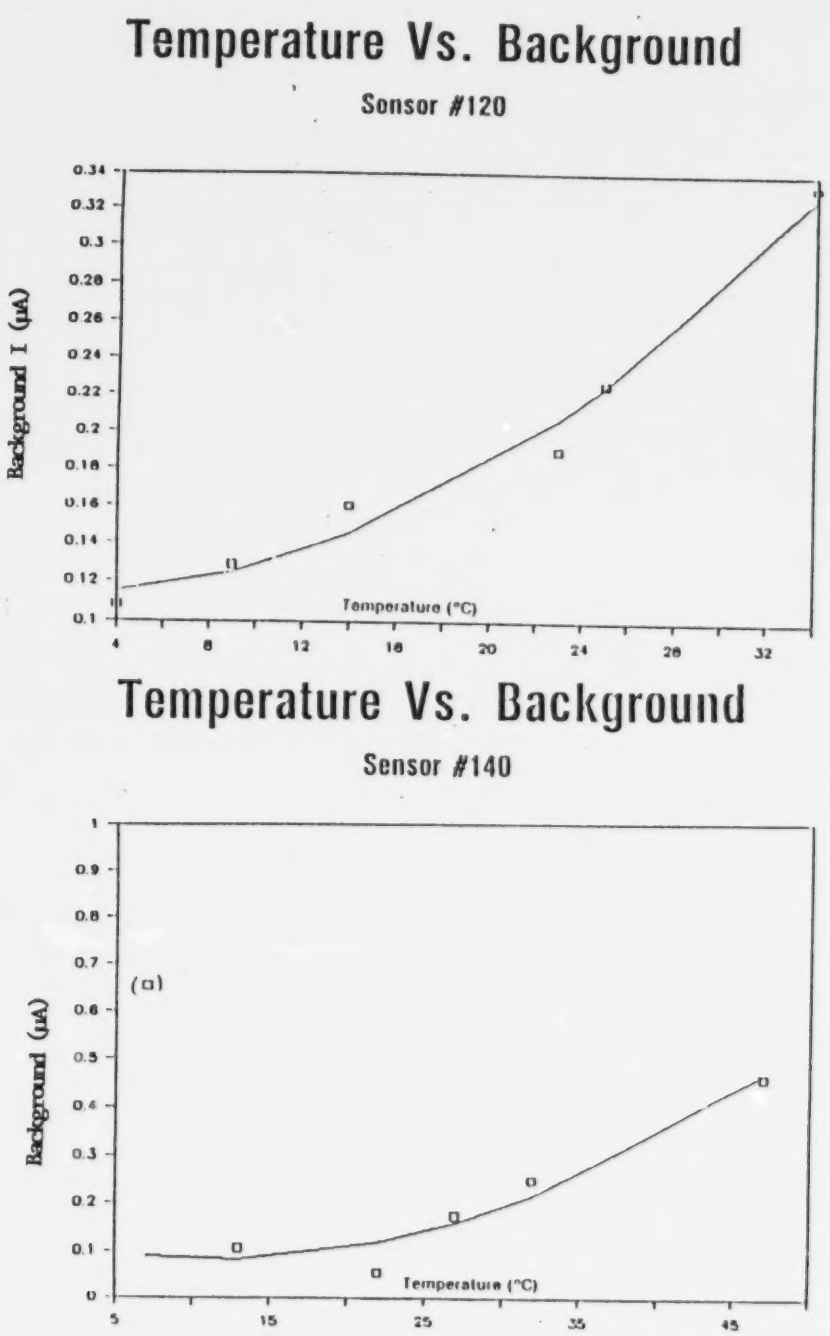
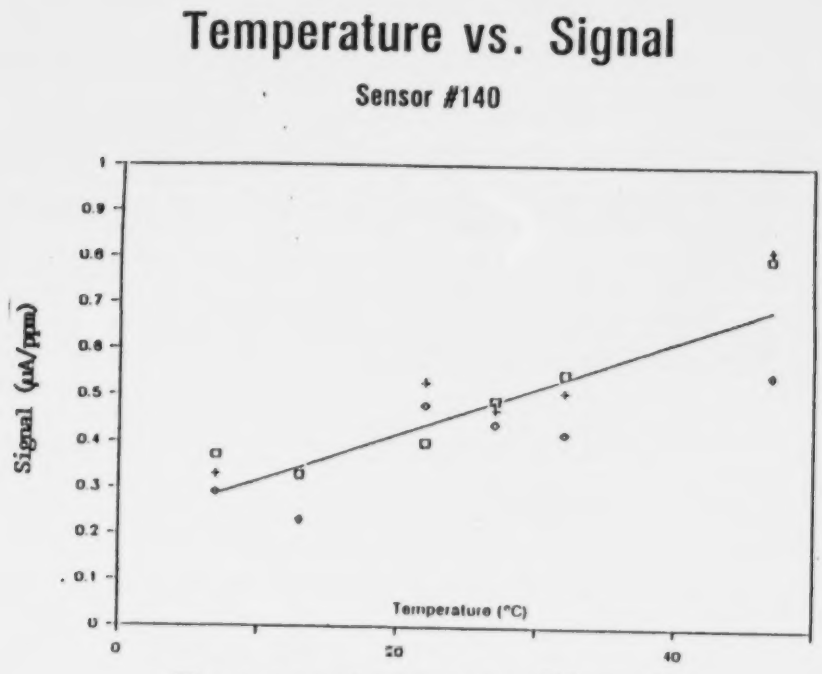


Figure 10: Effect of temperature on the background signal of two different LSA sensors. The data fits the equation I (uA) = at^3 + b; (r^2 = 0.98)



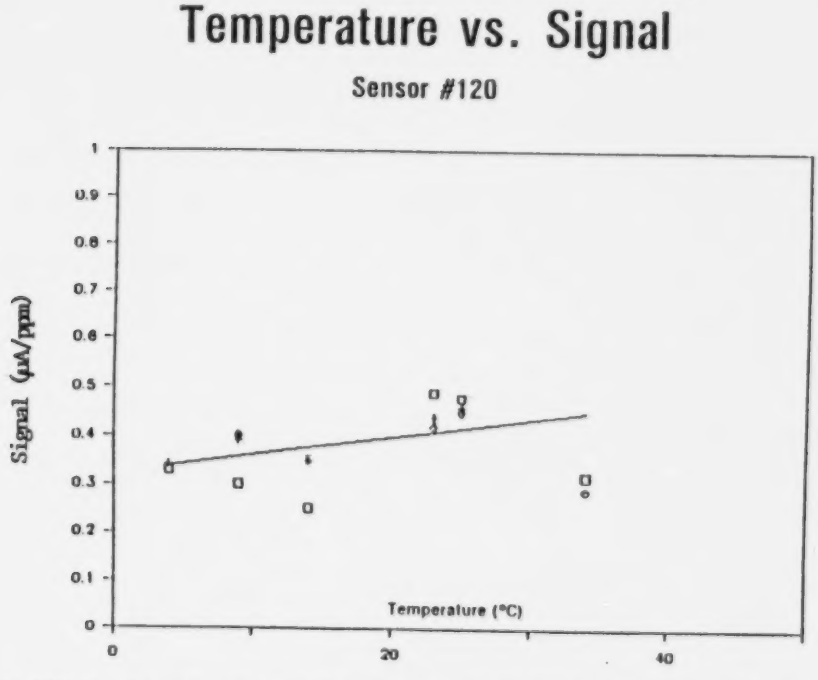


Figure 11: Effect of temperature on the sensitivity of two IAS sensors. The data fits the linear relation i = at + b. 0.46 ppm; +1.0 ppm; and 3.16 ppm.

The alternative method is to collect the uncompensated sensor data and simultaneously monitor the temperature. The data is then corrected for temperature effects mathematically, using calibration curves which may be readily generated for any type of sensor at any stage in the sensor lifetime.

The technique of recording the temperature data and using subsequent mathematical correction was chosen for this project for several reasons:

a) The operator would be able to examine the raw data and add to the confidence in the results.

b) The instrument would be more flexible, as different sensors may readily be installed without requiring any hardware changes,

c) The number of electronic components in the potentiostat circuit would be reduced to make it smaller,

d) It is scientifically preferred to make a measurement rather than to assume compensation is the same under all field conditions,

e) The temperature is a useful piece of data and may be desired for other reasons (e.g., to help define situations, exposures, unusual conditions, and doses),

f) Recording the temperature allows a flexible approach to the scientific experiment with different sensor systems, and

g) It is extremely easy to do and does not require compromise of monitor specifications (e.g., larger size, weight, ...).

The data in Figures 10 and 11 were used to calculate the coefficients for the temperature compensation equation for the TRI sensor:

For the background (or zero), the temperature compensation is described by the equation:

$$BG_o = BG_1 - aT^2 \quad \text{or} \quad BG_1 = BG_o + aT^2 \qquad (1)$$

For the span, the temperature compensation is described by the linear equation

$$i_o = i_1 - bT \qquad (2)$$

where the subscripts "0" and "1" refer to 0°C and the temperature of measurement, respectively,"BG" is the background current,"i" is the signal current, and "a" and "b" are constants (found by linear regression of the data from Figures 10 and 11).

The net signal at the temperature of measurement, i_1, is calculated by simply subtracting the background at the temperature of the measurement, BG_1, from the total signal, i_t:

$$i_1 = i_t - BG_o - aT^2 \qquad (3)$$

Equations (2) and (3) may be combined to allow correction of the signal back to the reference temperature, in this case 0°C. The resulting equation for temperature compensation of the signal is:

$$i_o = i_t - BG_o - aT^2 - bT \qquad (4)$$

(for sensors tested, a=0.00019, b=0.005 (#120) and 0.009 (#140))

It is envisioned that software can be written for the data logger to internally correct the signal.

NOTE: it is of interest to note that improved temperature characteristics may be possible by combining the TRI sensor with the diffusion (passive) sampling technology developed by EPA personnel at RTP. Future work could address the design of a sensor with a smaller or zero temperature coefficient.

Reproducibility (Precision):

Reproducibility of the sensor response after repeated exposures is of critical importance in the collection of reliable data in the field. The data shown in Figure 12 were collected from the same sensor over several hours before and after a number of exposures at different concentrations and as the temperature was changing. The experiment was started about 12 hours after the sensor was placed on bias and put in an oven at 40°C. Five hours after beginning the test, the temperature was decreased to 27°C. All of the data was collected using the Rustrak Model RR-400 data logger and a customized TRI cable assembly.

The zero drift of the sensor corresponds to approximately 300 ppb over a period of ten hours but is extremely obvious and can be easily corrected. The span drift was less than 5% during this interval. With periodic measurement of the sensor zero, correction for drift to a few per cent of signal could be made. These data indicate that the sensor zero needs to be measured periodically until the background is stable (perhaps 24-36 hours may be required for ppb level measurements). After sensor stabilization (see Figure 12), it may be necessary to measure the background less frequently.

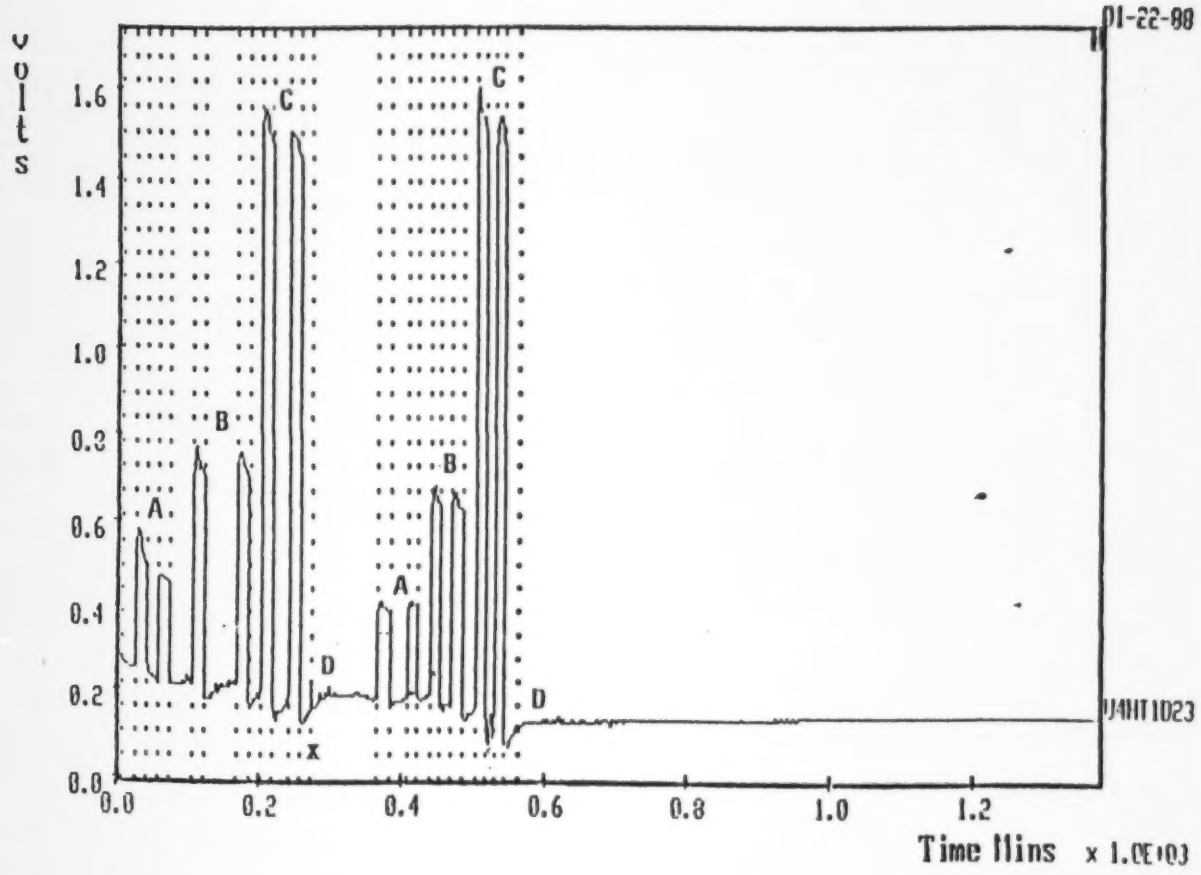


Figure 12: Long term response of LSA sensor. Data collection began 6 hours after putting sensor on bias. A = 0.46 ppm, B = 1.0 ppm, C = 3.16 ppm; D = lab air; X = temperature change from 32° C to 25° C.

Sensor zero drift is a major limit for low-level real-time monitoring and the data logger (planned for FY88) with "auto zero" will improve the field data collected with the instrument. In fact, the maximum accuracy for the NO_2 monitor (minimum zero drift) will be obtained by allowing the sensor to remain "on" (pump can be "off") for at least two days before it will be used in the field (e.g., perhaps over a weekend). Thus, if the unit is powered by a rechargeable 9 V battery, it may operated from the battery for up to 24 hrs and then plugged into the charger whenever not in use with the sensor switch always "on." Sensor background has been observed to decrease to several nanoamps after being "on" continuously for a week or more.

Long Term Stability (sensor lifetime):

One TRI attitude-insensitive sensor was tested under continuous air flow conditions to determine the lifetime and stability of the sensor. The rate of evaporation of the electrolyte from the sensor was measured by weighing the sensor each day and recording the weight lost. The weight loss of the sensor is primarily due to the evaporation of the water in the electrolyte in the relatively dry (30-50 % RH) laboratory air that is being circulated through the sensor at 100 cc/min. The evaporation of electrolyte is a major factor in determining the lifetime of the sensor. The results of this lifetest are shown in Figure 13. The weight loss was initially 0.16 g/day but decreased to 0.11 g/day after 5 days. During the test, the sensor signal remained very stable at 0.18 ± 0.004 μA/ppm. After 5 days on continuous bias, the background of the sensor decreased to just 10-20 ppb. The signal/noise ratio, background current, and response time exhibited marked improvement with time. The sensor response to NO_2 is actually much better on day 20 of the test than on day 5 (see Figure 13b and 13c). This confirms the fact that it is optimum to keep the sensor "on" continuously for most stable performance.

Selectivity:

Several potential interfering gases were tested under the conditions to be used in the instrument (-200 mV potential; 100 cc/min flow rate). These data are summarized in Table 4 in the tentative specifications for the LSA sensor. Only H_2S exhibits a substantial signal. A lead-acetate scrubber effectively removes the sulfur compounds, while not affecting the NO_2 response. This scrubber was incorporated into the final design of the instrument and several have been included with the prototypes for evaluation by the EPA. The filter is attached to the outside of the unit because it will only be needed if the ambient to be sampled is expected to contain H_2S. Additional interference tests should be included in future work.

13a)

Lifetime Test Results

(TRI Attitutde Insensitive LSA Sensor)

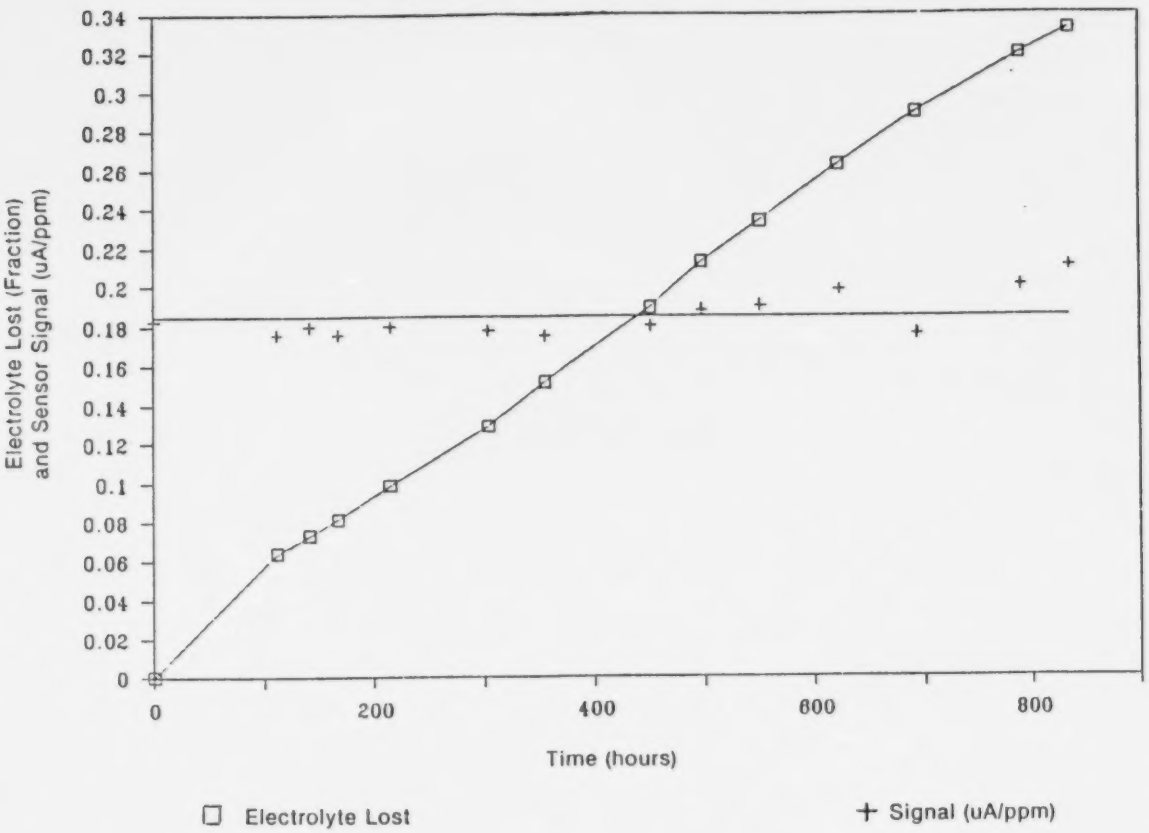
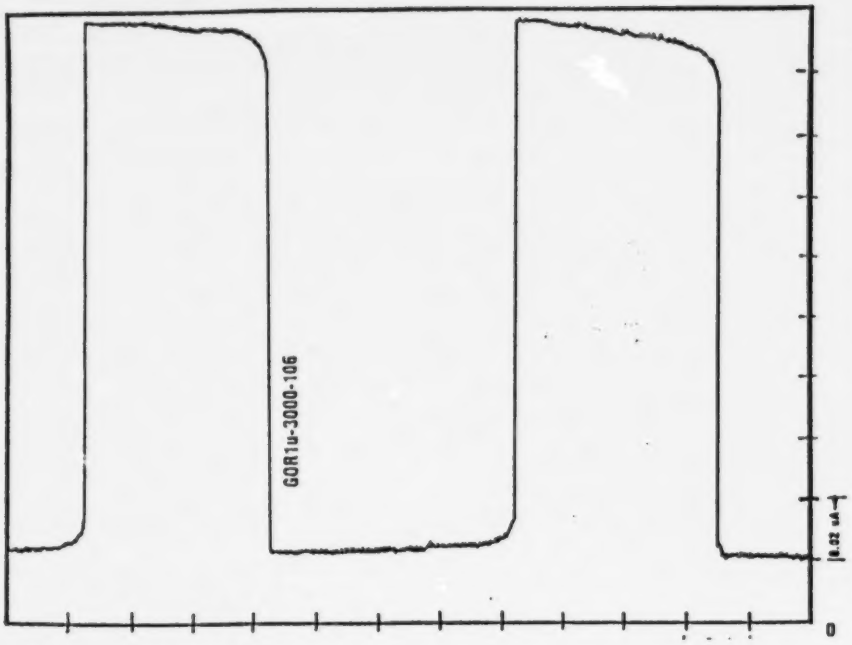


Figure 13a: Lifetest of Gortex LSA sensor for first 30 days of operation. Continuous air flow at 100 cc/min. of room air. After 30 days, sensor had lost 30 percent of the electrolyte volume, but signal is virtually unchanged.

13b) Response on Day 5



13c) Response on Day 20

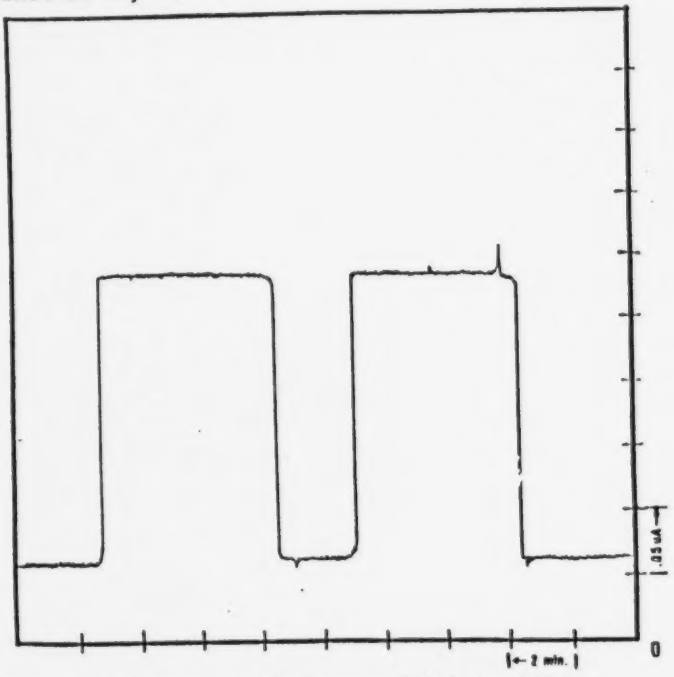


Figure 13 (cont'd.): Response of test sensor 106 during lifetest.
b) Day 5; I = 0.176 uA/ppm. c) Day 20; I = 0.18 uA/ppm.
Flow = 100 cc/min.; Bias = -200 mV vs pt/air.

TABLE 4: TRI NO_2 Sensor Preliminary Specifications

Range (switch selectable) : 0-1 ppm and 0-50 ppm
Response Time (0-90%): <30 sec
Recovery Time (100-10%): <30 sec
Reproducibility: Better than 5% over 8 hours
Signal/Noise @ 1ppm: >100:1
Background: 00.1-0.25 ppm
Stability: Zero Drift - (after 12 hours) 100 ppb /8 hours.
(after 36 hours) 20 ppb/8 hours.
Span Drift - < 5% F.S. in 8 hours.
Temperature Drift - 10-20 ppb/^{o}C
Humidity Range: 0-100%: 5-95% continuous
Sensor Lifetime: > 3 months continuous*; design goal is 1 year.
Interferences (ppm:ppm NO_2):
H_2S: -0.33:1 (w/o filter); > -100:1 with filter
CO: >-10000:1 w/o filter
NO: none
EtOH: > -1000:1 w/o filter
NH_3: Not tested

* Continuous tests have been performed for 1 1/2 months; and expectation of 1 year lifetime is apparently very reasonable for this sensor design.

CONSTRUCTION OF INSTRUMENT

Technical Discussion:

The instrument involved the design of several new circuits in order to interface the conventional potentiostat circuit to a variety of data logger systems and to operate the unit from a simple 9 V battery. Three new circuits designed during this work included the power supply, temperature sensor, and pump control circuits. A layout and schematic for the final circuit are given in the instrument manual for the prototype (14).

A pump control circuit capable of computer operation of pump direction at a single but adjustable speed was designed. However, the tests of the circuit revealed that it requires about 7.2 V and 100-250 mA to operate. This increases the instrument power requirement, and would call for a large battery pack. Also, the pump speed could not be easily adjusted to a low flow rate (100 cc/min.). For these reasons this circuit was abandoned and is not included in the prototype instruments. The pump in the prototype is powered by a single battery (D-cell) external to the unit and the flow through the sensor is adjusted with a simple "leak" valve located on the pump inlet. A circuit lower in power and more versatile computer-controlled pump controller will be designed in the field unit (FY88).

The low power pump (Spectrex AS-400) operates on voltages as low as 1.0 V and currents as low as 20 mA. A single rechargeable D-cell lasts 72-100 hours of operation and an alkaline battery would last 3-4 times longer. Figure 14 is a graphic representation of the battery voltage and air flow vs. time for a pump under continuous operation in the prototype instrument. The bleed or "leak valve on the pump inlet allows operation of the unit from a few cc/min to over 1 L/min.

The pump direction is not reversible in the prototype instrument and new operating protocol was developed to zero the instrument. At periodic intervals, a gas scrubber, or "zero-filter", is attached to the sample inlet. The zero signal is collected for a few minutes and the zero filter removed to continue monitoring. The zero data is bracketed in the data logger using the event marker. The condition of the zero-filter is monitored by observing a color change in the filter bed material to make sure it is fresh. In FY88, an "auto-zero" feature will be installed in the unit.

The potentiostat circuit board has three new circuits. These provide for: 1) conversion of 9 VDC to ± 5.35 VDC, 2) use of the ± 5 VDC to create a very stable ± 2.5 VDC for reference potential and eliminating the mercury battery, and 3) a temperature independent zero adjust control (offset voltage for the output). In addition, provision was made for readout,

Pump Battery Capacity

Rechargeable D-Cell, I = 30 mA

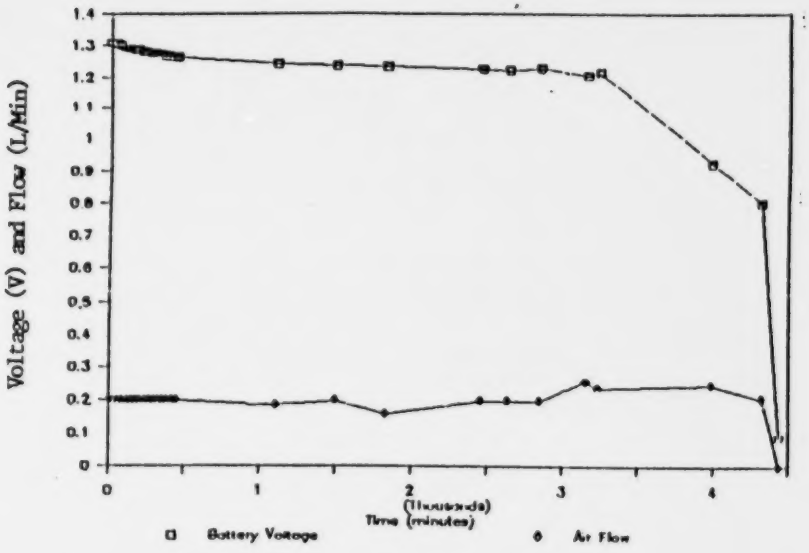


Figure 14: Test of pump battery capacity, measured as battery voltage and air flow rate (cc/min.). Lifetime of fully charged Ni-Cd D-cell is approximately 72 hrs.

adjustable span control, digital "range" switching, and manual control of pump/range/power control options. This new circuitry adds stability to the instrument as well as increases flexibility of operating the unit with different sensors and computer systems. The temperature sensor, an AD590, is also located on the circuit card and uses the stabilized voltages for operation. (NOTE: the temperature sensor will be moved to the sensor housing in future designs.)

To perform ppb-level measurements, it is critical that the instrument circuitry be virtually free of noise and drift. The detection limit of the instrument will then be limited solely by the performance of the sensor (the ideal situation and our goal). Capacitor and low-pass RC filtering was used on all power supplies. Low noise, low offset, and low drift (especially with temperature) circuit components were specified in circuit design.

The major challenges during this task were: 1.) to lay out the new circuits (ground planes and ground loops were designed around the potentiostat to reduce potential noise) in the minimum board space, 2.) debug all the features with as many variations (sensors and signal levels) as possible, and 3.) interface to the optimized sensor to a data logger to provide a practical system for field monitoring of NO_2. This new circuit was evaluated and used to acquire much of the data presented in this report.

General Description of the Instrument

Block Diagram of the Prototype NO_2 Personal Monitor are shown in Figures 15 and 16. This unit contains all of the features in our design objectives and consists of three modules. Module 1 is the detector, measuring temperature and ppbV levels of NO_2. Module 2 is a Rustrak Ranger data logger system, which is interfaced by a 15-pin connector and cable to Module 1. Module 3 is the battery pack, consisting of a single D-size cell for pump operation (power for circuit operation is contained in the 9-volt battery contained within Module 1).

The instrument itself is the largest module, at approximately 5" x 7" x 2¼" and slightly less than 1.5 pounds. The battery plugs into the jack provided in the side of the case. The instrument is connected to the data logger via a light-weight extendable cable. The data logger (RR-400) is approximately 3" x 5½" x 1½", with an LCD display which provides continuous readout of the desired data channel. The entire assembly of 3 modules weighs about 3 pounds and, if packaged into a single case, could weigh closer to 2 pounds.

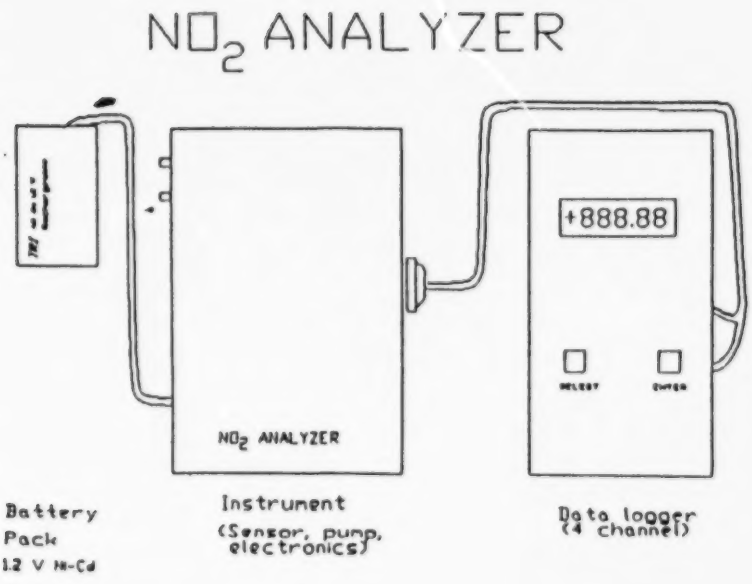


Figure 15: NO_2 instrument at the end of this phase of the project, showing the three modules and connectors.

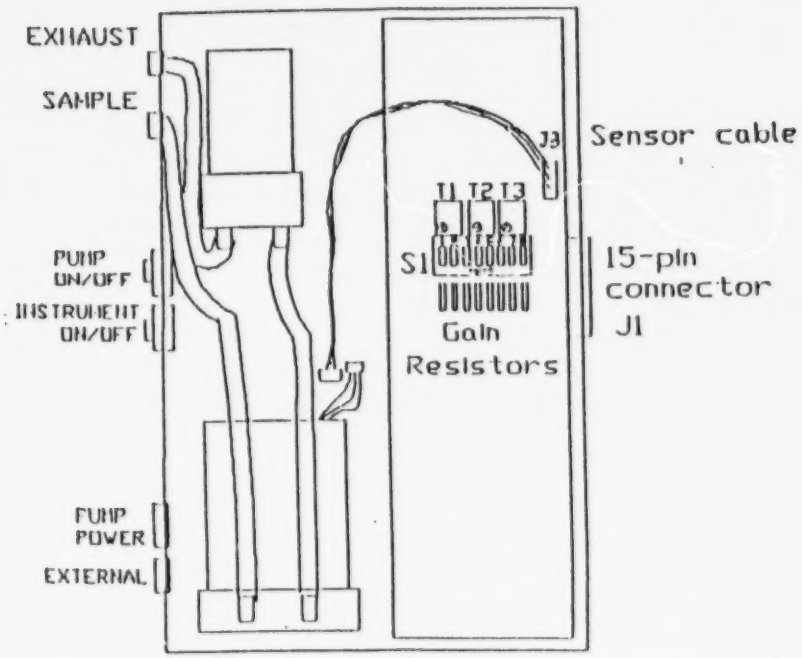


Figure 16: Lower board of NO_2 instrument electronic circuit illustrating location of gain switch, sensor connection and bias and offset adjustment potentiometer.

PRINCIPLES OF OPERATION OF ANALYZER AND DATA LOGGER

The following section provides a general discussion of the operation of the instrument. Detailed instructions are given in instrument manual for the prototype (14).

The sensor is connected to the potentiostat circuit card via the 3-connector cable leading from connector J3 on the lower circuit board (see Figure 16). The potentiostat circuit provides the ability to set the thermodynamic potential of the sensing electrode as well as convert the current generated by the sensor into a voltage for further amplification and subsequent recording. The potentiostat circuit holds the potential of the working electrode constant relative to a reference electrode regardless of the current passing through the sensor. It is critical that the potential be held constant since small fluctuations in the bias may cause substantial changes in the sensor background or signal currents.

The current is directly proportional to the concentration of the analyte gas in the exposure chamber of the sensor. This current is converted to a voltage signal by passing it through a known and fixed feedback (gain) resistor. The output of the circuit is sent to the connector J1, where it can be measured by any high impedance voltage measuring device, such as a recorder or voltmeter. The output of the potentiostat is sent to a differential amplifier circuit to condition the signal, perform offset adjustment, and provide the buffered output voltage signal for recording or display.

All the pertinent voltages from the instrument can be measured at the connector J. These include sensor bias, battery voltages, and the output of the sensors. A cable is used to interface the NO_2 monitoring module with any suitable data collecting device.

Sensor Installation and calibration:

The sensors provided with the instrument have an estimated operating lifetime of one year (6 months minimum) when operated under continuous or intermittent conditions. The sample must be humidified when operating continuously over long time periods.

The sensor lifetime is controlled largely by the rate of evaporation of water from the electrolyte through the membrane. The evaporation rate of electrolyte is a function of the working electrode area, membrane porosity, sample humidity, and sample flow rate. TRI is currently investigating several methods of increasing the sensor lifetime while maintaining the small sensor size.

The sensor is replaced when it is no longer possible to calibrate the signal, the magnitude of the background is excessive, or the signal stability is unacceptable. Sensor replacement is accomplished by removing the cover of the instrument and separating the sensor electrical and pneumatic connections as described in the instrument manual for the prototype (14). The new sensor is connected and installed in the sensor clip following the reverse procedure.

After allowing the new sensor to stabilize for 5-10 minutes and setting the gain to minimum (DIP positions 1 & 7 are on), the zero offset is adjusted to a small, positive value (this only needs to be done if the circuit has been changed because a factory adjustment has already been made). The small positive value is used for the "zero signal" level so that you can always tell that your unit is operating and can read small negative interferences, should they occur. The DIP switch is returned to its proper value (6 & 7 "on" is typical for ppb measurements) and when the sensor background has stabilized to a low value, the data logger is connected and you are ready for field measurements. (If data is required with ppb sensitivity, the sensor should be left "on" overnight before sampling begins. This will allow the background signal to stabilize, and minimize drift at the high amplification required.)

Collecting and storing data:

The data is collected from the instrument by the data logger. As illustrated in the instrument manual (14) and Figures 15 and 16, all instrument signals are measured at the 15-pin connector on the right side panel of the instrument. The data logger may collect up to four channels of data, although the cables prepared allow for only two channels to be measured. The first channel is the output from the electrochemical sensor and the second the output of the temperature measurement channel. The data logger illustrated herein is the Rustrak RR-400 unit.

The analog signals from the sensors are converted to digital signals every 690 msec by the data logger. Data is averaged and stored in the data logger memory at a rate determined by the number of channels and length of the data recording session selected by the user (see Rustrak Manual for details).

The data logger must be programmed before the initial use and every time the power is turned off. This consists of defining the sensor type for the two channels to be used (0-2 V range, called Type 13 by Rustrak) and the length of the data acquisition, or recording, session. Once these parameters are entered, the recording session may be started at any time.

Use of data analysis software:

The data analysis software provided with the Rustrak data logger is very versatile. It is a menu directed package that makes extensive use of the Function keys of the PC. Programming knowledge is not required to use the software.

EVALUATION OF PROTOTYPE INSTRUMENT (TEST RESULTS)

The three prototype units were tested and much of the sensor performance data was collected using the prototype instruments and the data loggers. Much of the graphics and data analysis was performed using the software provided with the data loggers. Tests were performed to evaluate the behavior of the instrument under a variety of simulated field conditions.

A typical set of NO_2 exposures at room temperature recorded with the data loggers are shown in Figure 17. These data were collected with Sensor 140 over a period of 10 hours using several concentrations of NO_2. Using the "Integrate" function of the data logger software, the areas under the peaks were calculated to be 9850 V-seconds, or 5.7 ppm-hours, using the gain of 1 V/μA and calibration factor for Sensor #140 of 0.48 μA/ppm at 32^{o}C. The actual total exposure, based upon the known concentration of the vapors and time each vapor was connected, is 5.0 ppm-hr. This gives an error of 14% for the measured exposure over 10 hours and a temperature range of 5^{o}C. These data were not corrected for temperature or baseline drift and are indicative of data collected under changing environmental conditions.

Measurements were performed to determine the effect of temperature upon instrument and sensor, independently. The sensor was connected to the unit with a 12" cable. This allowed variation of the instrument temperature while the sensor temperature was held constant. Figure 18 shows the background and noise for Sensor #140 at room temperature while the instrument was at 23^{o}C and 40^{o}C. There is virtually no change in the performance of the instrument with changing temperature. However, when the sensor temperature is changed, the background and span can change. The changes in span are small compared to the background changes in the sensor. Measurement of the temperature and the planned "auto-zero" function should provide adequate compensation for these variations and virtually eliminate errors due to temperature changes.

The response of the temperature sensor circuit was designed to be 10 mV/^{o}C. A calibration curve was performed for the range 3^{o} to 45^{o}C, and is shown in Figure 19. The slope of the line is actually 7.5 mV/^{o}C, with the offset voltage of the unit adjusted so that 23^{o}C corresponds to 1.000 V output to the data logger. This sensor circuit should be corrected.

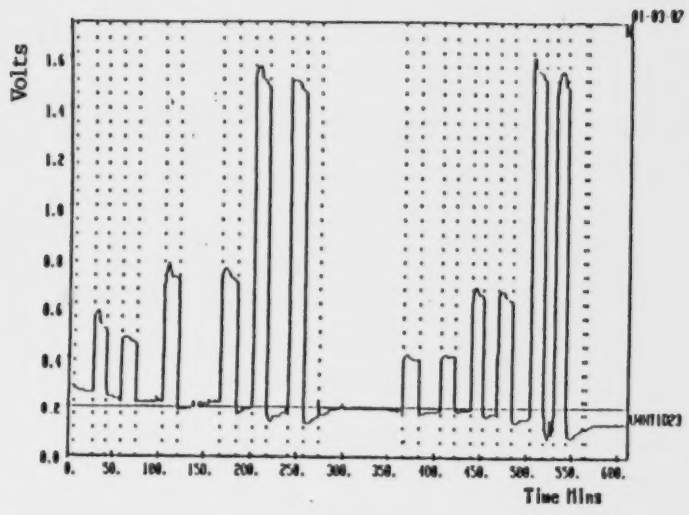


Figure 17: Plot of simulated 10-hour exposure, comparing calculated exposure (8600 V-sec) with known exposure (9850 V-sec).

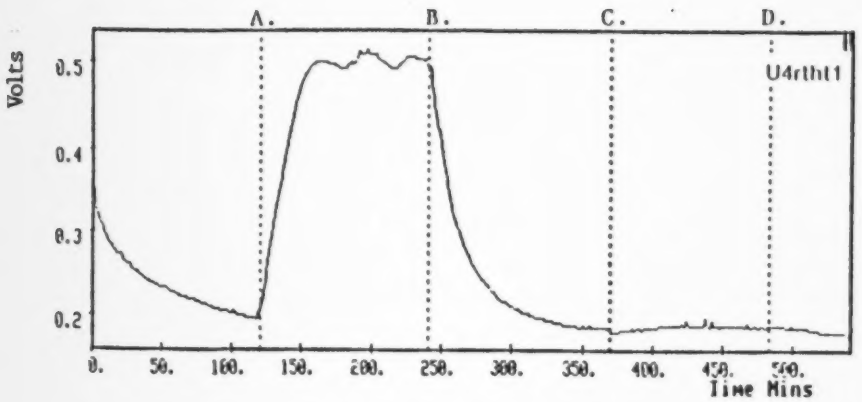


Figure 18: Effect of temperature on instrument background:
A. Sensor placed in oven at 36° C, unit at room temperature (22° C).
B. Sensor and unit at room temperature (22° C)
C. Sensor at room temperature, unit in oven at 36° C.

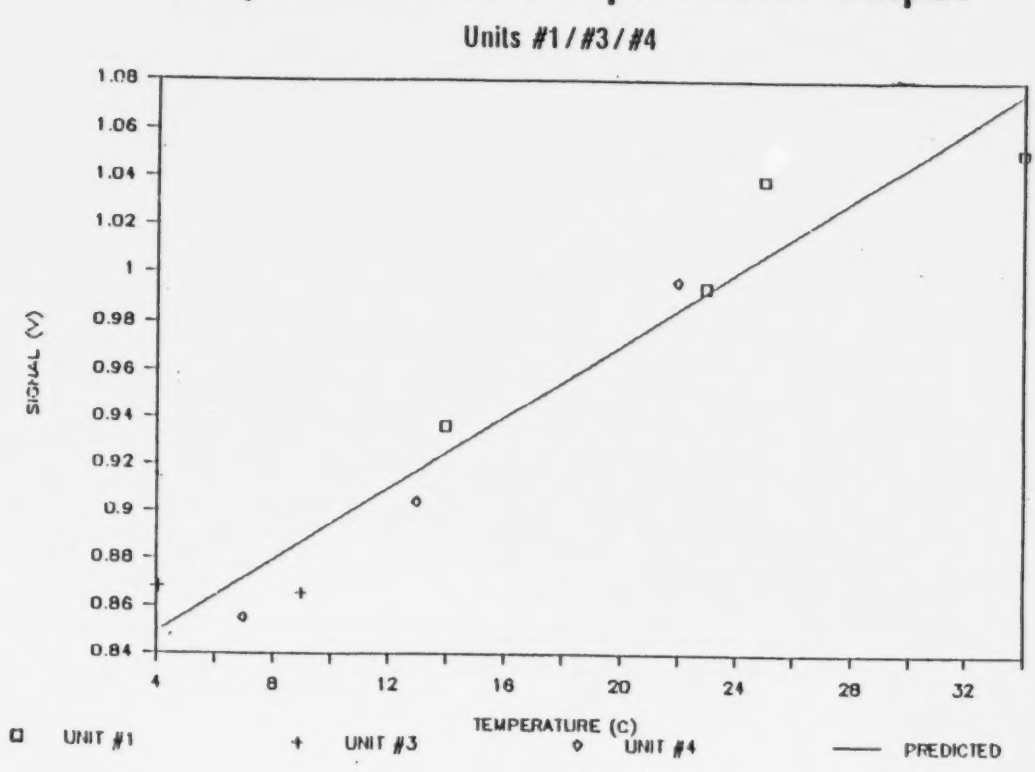


Figure 19: Calibration curve for temperature sensor. Temperature data was collected using mercury thermometer during actual testing of instrument response to NO_x. Thermometer was aboul 30 cm above instrument.

The rate of change of the sensor background with changing temperature is slower than the rate of change of the temperature sensor signal. Under conditions of rapid, large fluctuations in the ambient temperature, this could cause inaccurate temperature correction. The difference in rate of response of the two sensors is due to the fact that the low mass temperature sensor was following the temperature of the circuit board to which it was soldered. The electrochemical sensor, however, takes longer to respond to temperature changes.

The temperature sensor was removed from the circuit board of and embedded in the housing of the electrochemical sensor, near the gas exposure chamber. This instrument was then placed in a 40^{o}C oven, and the output of both the electrochemical and temperature sensors were recorded on a data logger. A zero filter and a sample of 1 ppm NO_2 were attached periodically to the unit inlet to determine sensor span and zero as a function of recorded temperature as the temperature changed. These data are presented graphically in Figure 20 and indicate that the response of the sensor is related not so much to the sample (air) temperature, but to the temperature of the sensor. It is apparent that the best temperature compensation will be achieved when the temperature sensor is embedded into the sensor housing near the working electrode. This will be accomplished in FY88 work.

Estimates of battery lifetimes can be made by using the measurements of Volts and Amperes consumed by the unit under different conditions:

Pump batteries - The pump consumes 25-30 mA at 1.2 V. For fully charged D-cells with a capacity of 4.4 Ah, this corresponds to 100-150 hours of operation. Data from several of the units indicate an actual operational time of 75-100 hours for a fully charged battery. The rated capacity of a NiCd is rarely achieved in practice.

Instrument batteries - The electronic circuits of the analyzer consume 1.5 to 2.0 mA of current. This would allow more than 30 hours of operation using a rechargeable 9 V battery and more than 200 hours using an alkaline battery. Two batteries in parallel are not recommended since standard alkaline batteries do not all discharge at the same rate. A single battery is therefore the recommended configuration and the second battery position is provided so that the unit can remain powered when the batteries are changed.

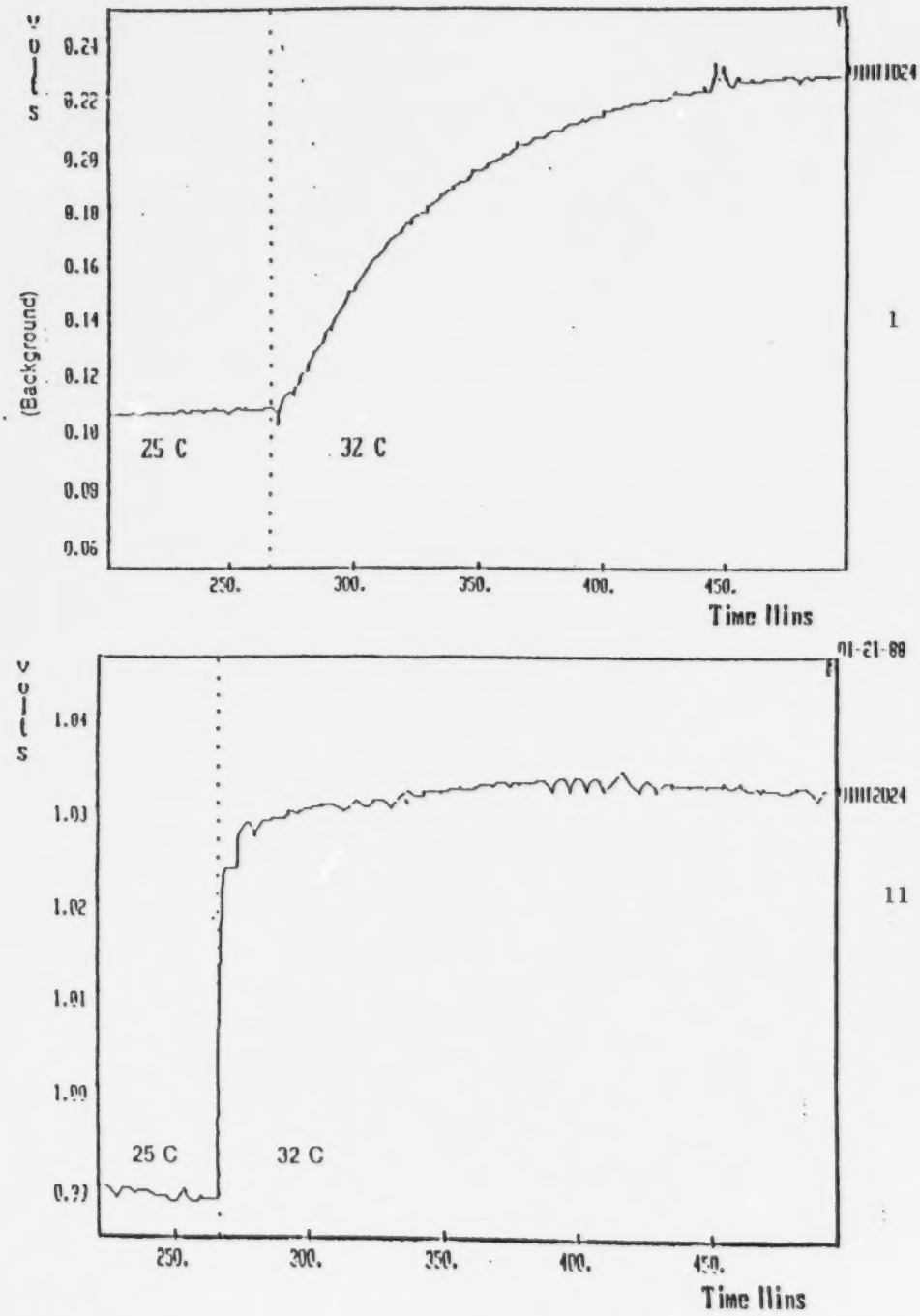


Figure 20a): Response of NO_2 sensor (1) and temperature sensor (11) to a step change in instrument temperature. Temperature sensor mounted on circuit board.

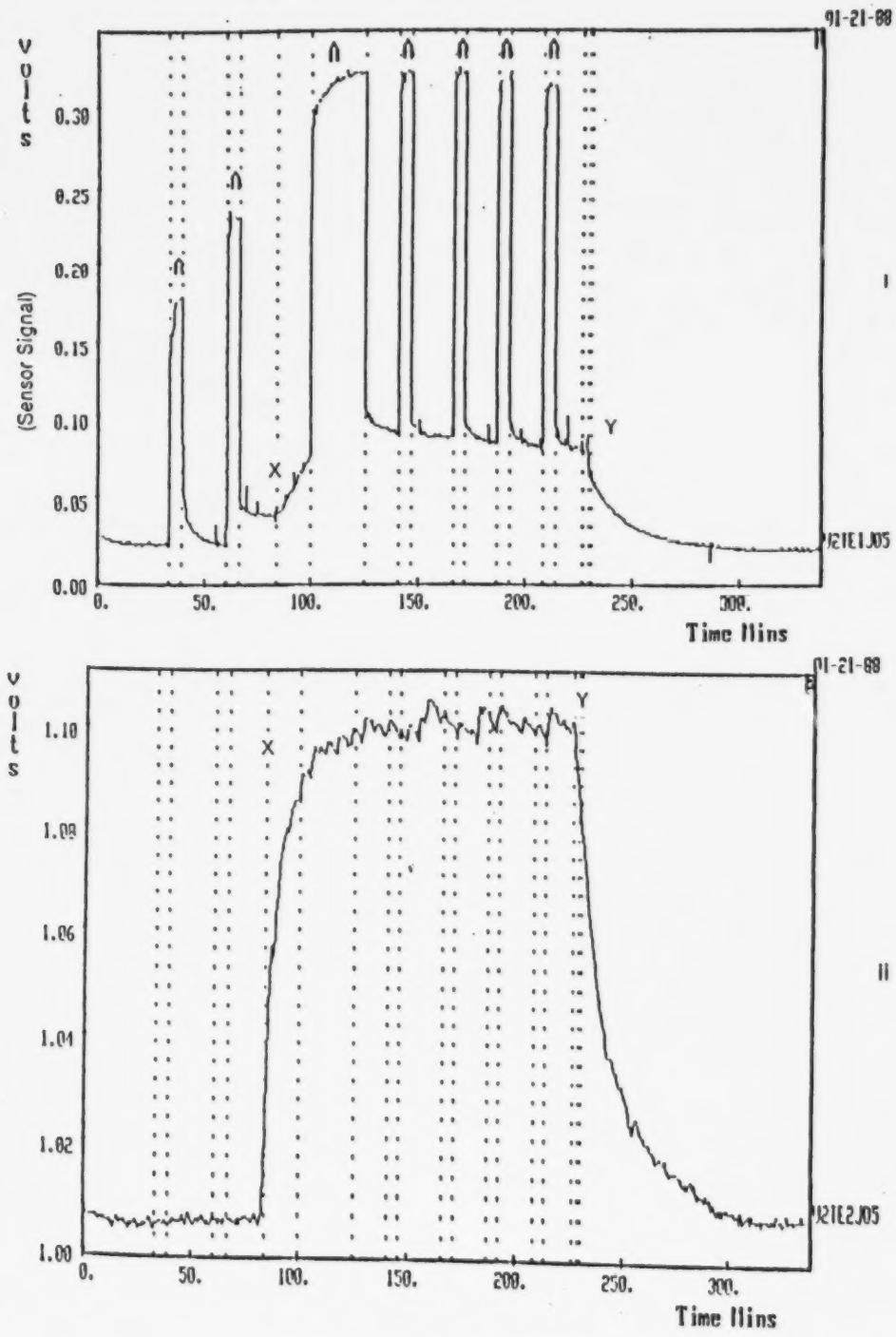


Figure 20b): Response of NO_2 sensor (I) and temperature sensor (II) to a step change in instrument temperature: x = 25 to 40° C and Y = 40 to 25° C. Temperature sensor mounted in NO_2 sensor housing.

Data logger batteries - the data logger was operated for up to 48 hours using two channels on the three AA rechargeable internal batteries. It is recommended that the data loggers be recharged each evening or used with the battery charger whenever possible.

Initial attempts to improve the sensor are illustrated in Figure 21 wherein the response of two sensors to 1 ppm NO_2 are shown. Both sensors have an increased catalyst loading over the initial LSA sensor tested earlier. There is no visible decay in the signal, signals are higher, and the signal to noise ratio is virtually as high as for the LSA sensor discussed herein. After addition of additional catalyst, the sensors were conditioned so that all trace impurities in the electrode and electrolyte were removed.

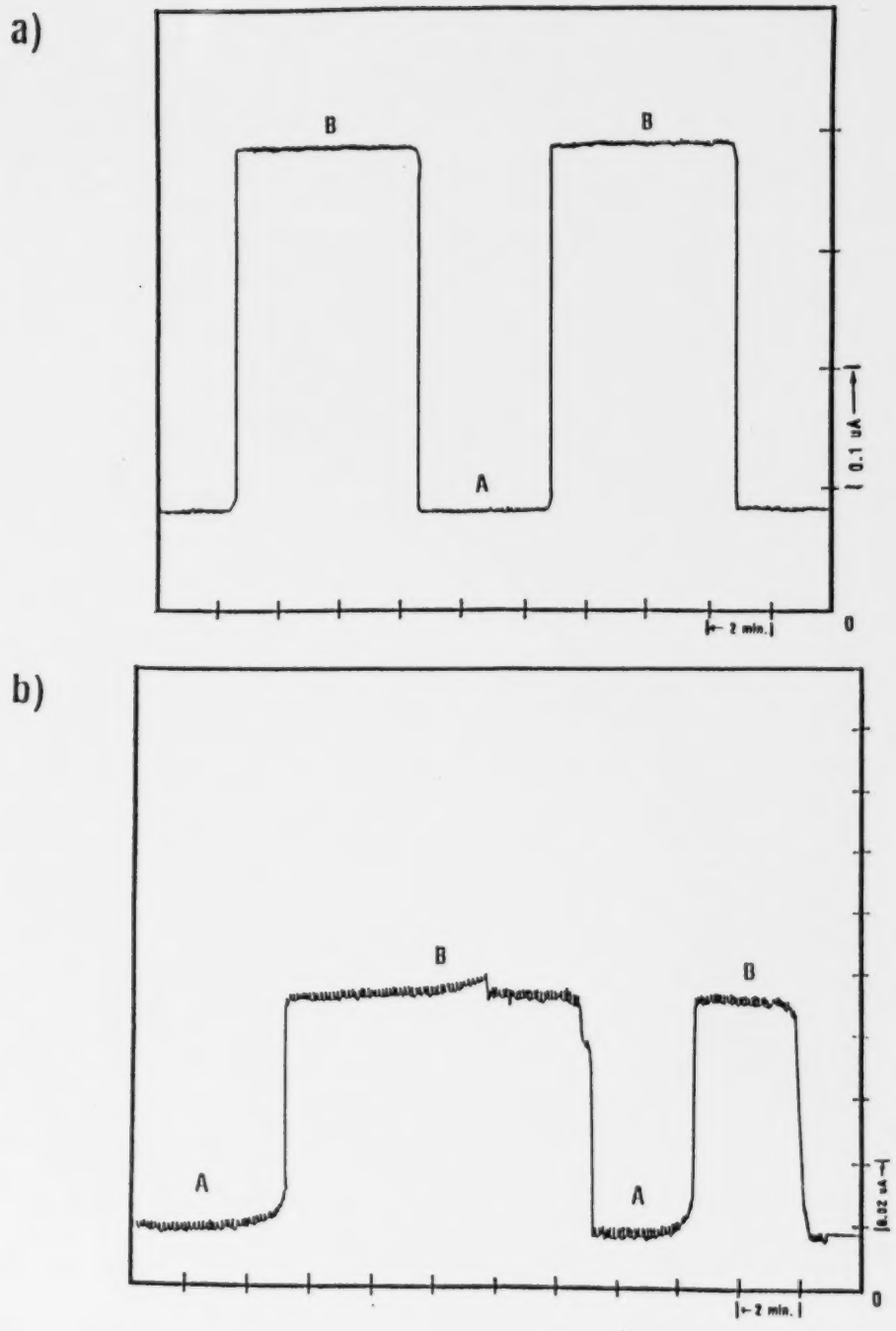


Figure 21: Response of two TRI LSA sensors to 1 ppm NO_2 after additional catalyst loading. A = background; B = 1 ppm NO_2.

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